UNIT 11

HYDROXY COMPOUNDS AND ETHERS

Alfred Bernhard Nobel

Alfred Bernhard Nobel was a Swedish chemist, engineer, inventor, and philanthropist. Nobel found that when nitroglycerine was incorporated in an inert absorbent like kieselguhr (diatomaceous earth) it became safer and more convenient to handle. He patented this mixture in 1867 as "dynamite". Nobel prizes were established in accordance with his will. The Noble prizes is considered as one of the precious awards in the fields of chemistry, literature, peace activism, physics, Economics and physiology or medicine.

KOMWX

Learning Objectives

After studying this unit the student will be able to

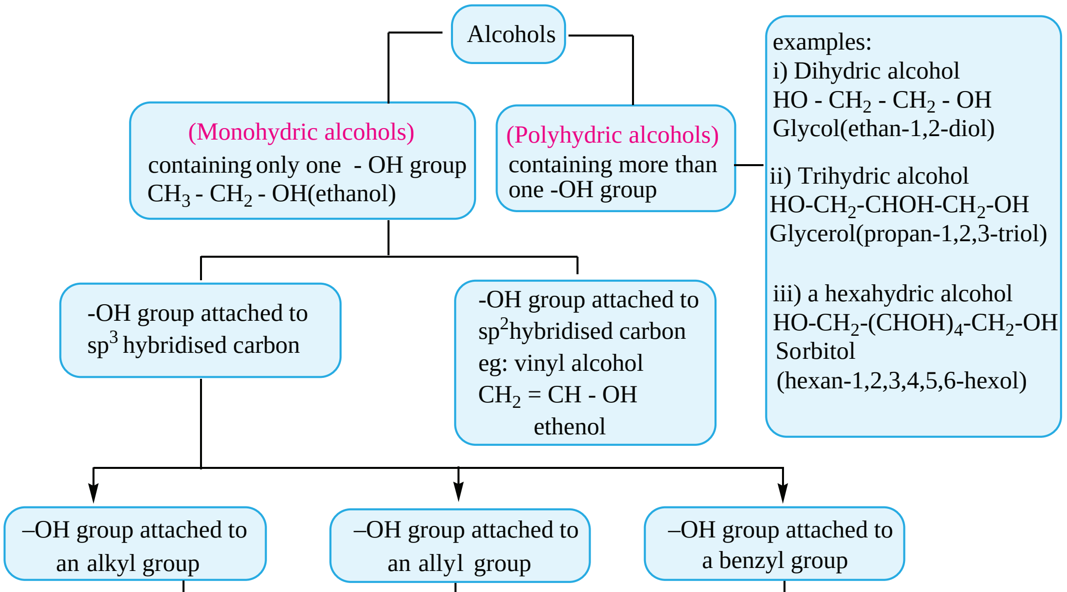
- describe the important methods of preparation and reactions of alcohols
- explain the mechanism of Nucleophilic substitution reaction of alcohols and ethers.
- explain the elimination reaction of alcohols.
- describe the preparation and properties of phenols
- discuss the preparation of ethers and explain their chemical reactions.
- recognise the uses of alcohols and ethers

INTRODUCTION

We have already learnt in eleventh standard that the hydrolysis of an alkyl halide gives an alcohol, an organic compound containing hydroxyl (-OH) functional group. Many organic compounds containing –OH group play an important role in our body. For example, cholesteryl alcohol commonly known as cholesterol is an important component in our cell membrane. Retinol, the storage form of vitamin A, finds application in proper functioning of our eyes. Alcohols also find application in many areas like medicine, industry, etc., For example, methanol is used as an industrial solvent, ethyl alcohol an additive to petrol, isopropyl alcohol as a skin cleanser for injection, etc., The hydroxyl group of alcohol can be converted to many other functional groups. Hence, alcohols are important resource in synthetic organic chemistry. In this unit, we will learn the preparation, properties and uses of alcohols, phenols and ethers.

11.1 Classification of alcohols:

Alcohols can be classified based on the number of hydroxyl groups and the nature of the carbon to which the functional group (–OH) is attached.



1° alcohol	$CH_3-\overset{H}{\underset{H}{C}}-OH$ ethanol	$\overset{3}{C}H_2=\overset{2}{C}H-\overset{1}{C}H_2-OH$ Prop-2-en-1-ol	$C_6H_5-CH_2-OH$ Phenylmethanol
2°alcohol	$CH_3-\overset{CH_3}{\underset{H}{C}}-OH$ propan-2-ol	$\underset{4}{CH_2}=\underset{3}{CH}-\overset{{}^1CH_3}{\underset{2}{CH}}-OH$ but-3-en-2-ol	$C_6H_5-\overset{1}{\underset{\underset{2}{CH_3}}{CH}}-OH$ 1-phenylethanol
3°alcohol	$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OH$ 2-methylpropan-2-ol	$\overset{4}{C}H_2=\overset{3}{C}H-\overset{{}_1CH_3}{\underset{CH_3}{\overset{2}{C}}}-OH$ 2-methylbut-3-en-2-ol	$C_6H_5-\overset{{}_1CH_3}{\underset{{}_3CH_3}{\overset{2}{C}}}-OH$ 2-phenylpropan-2-ol

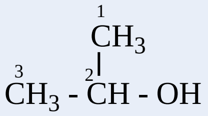
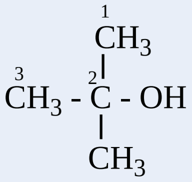
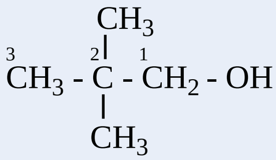
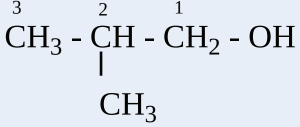
11.2 IUPAC Nomenclature

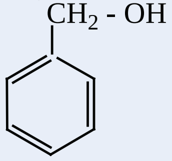
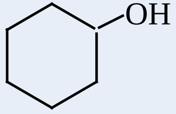
We have already learnt about naming the organic compounds according to IUPAC guidelines in XI standard. Let us recall the basic rules to name the alcohols.

1. Select the longest continuous chain of carbon atoms (root word) containing the functional group (-OH).
2. Number the carbon atoms in the chain so that the carbon bearing the -OH group has the lowest possible number.
3. Name the substituent (if any)
4. Write the name of the alcohol as below.

Prefix	+ Root word +	Primary suffix	+ Secondary suffix
(substituents)	(longest chain)	(Saturation /unsaturation)	(ol)

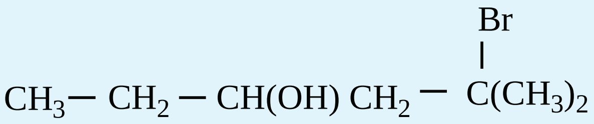
The following table illustrates the IUPAC nomenclature of alcohols.

Compound (common name, Structural formula, IUPAC Name)	IUPAC Name			
	Prefix with position number	**Root used**	**Primary suffix**	**Secondary Suffix**
Isopropyl alcohol  $\begin{array}{c} \overset{1}{CH_3} \\ \vert \\ \overset{3}{CH_3} - \overset{2}{CH} - OH \end{array}$ Propan-2-ol	-	Prop	an$\cancel{e}$	2-ol
Tertiary butyl alcohol  $\begin{array}{c} \overset{1}{CH_3} \\ \vert \\ \overset{3}{CH_3} - \overset{2}{C} - OH \\ \vert \\ CH_3 \end{array}$ 2-methylpropan-2-ol	2-methyl	Prop	an$\cancel{e}$	2-ol
Neopentyl alcohol  $\begin{array}{c} CH_3 \\ \vert \\ \overset{3}{CH_3} - \overset{2}{C} - \overset{1}{CH_2} - OH \\ \vert \\ CH_3 \end{array}$ 2,2-dimethylpropan-1-ol	2,2-dimethyl	Prop	an$\cancel{e}$	1-ol
Isobutyl alcohol  $\begin{array}{c} \overset{3}{CH_3} - \overset{2}{CH} - \overset{1}{CH_2} - OH \\ \vert \\ CH_3 \end{array}$ 2-methylpropan-1-ol	2-methyl	Prop	an$\cancel{e}$	1-ol

Benzyl alcohol  Phenylmethanol	Phenyl	Meth	an~~e~~	ol
Allyl alcohol $\overset{3}{C}H_2=\overset{2}{C}H-\overset{1}{C}H_2-OH$ Prop-2-en-1-ol	-	Prop	2-en~~e~~	1-ol
Cyclohexyl alcohol  Cyclohexanol	-	Cyclohex	an~~e~~	ol
Glycerol $HO-CH_2-CH(OH)-CH_2-OH$ Propane – 1,2,3 – triol	-	Prop	ane	1,2,3 – triol

Evaluate Yourself:

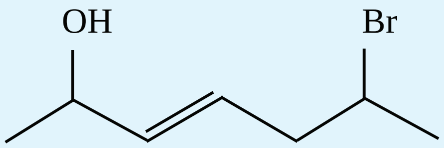
1. Classify the following alcohols as 1°, 2°, and 3° and give their IUPAC Names.

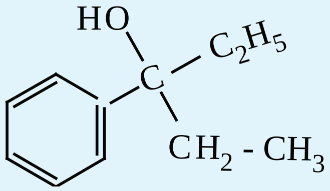
a) 

$CH_3-CH_2-CH(OH)CH_2-C(Br)(CH_3)_2$

b) $(C_2H_5)_3COH$

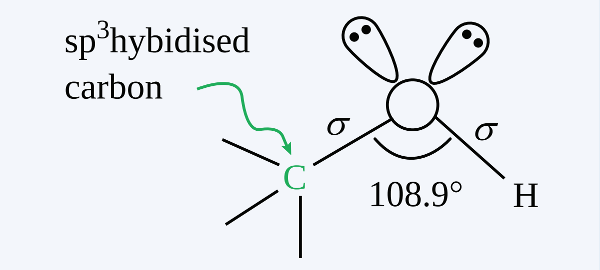
c) $CH_2=C(Cl)-CH(OH)CH_3$

d) 

e) 

2. Write all the possible isomers of an alcohol having the molecular formula $C_5H_{12}O$ and give their IUPAC names.

Structure of the functional group of alcohol.



The structure of -O-H group which is attached to a sp^3 hybridised carbon is similar to the structure of -O-H group attached to a hydrogen in water. i.e., 'V' shaped. In such alcohols, one of the sp^3 hybridised orbital of oxygen linearly overlap with the sp^3 hybridised orbital of carbon to form a C-O, 'σ' bond and another sp^3 hybridised orbital linearly overlap with 1s orbital of hydrogen to form a O-H 'σ' bond. The remaining two sp^3 hybridised orbitals of oxygen are occupied by two lone pairs of electrons. Due to the lone pair – lone pair repulsion, the C-O-H bond angle in methanol is reduced to 108.9° from the regular tetrahedral bond angle of 109.5°.

Preparation of alcohols:

We have already learnt that the nucleophilic substitution reactions of alkyl halides with dilute alkali, conversion of alkenes to alcohols by hydration and the preparation of alcohols using Grignard reagent in XI standard. These reactions are summarised below.

1. **From Alkyl halides:** Alkyl halides on heating with dilute aqueous NaOH gives alcohols. Primary alkyl halides undergo substitution by SN^2 reaction. Secondary and tertiary alkyl halides usually undergo nucleophilic substitution by SN^1 mechanism.

$$R\text{-}X + NaOH(aq) \xrightarrow{\Delta} R\text{-}OH + NaX$$

If R =t-butyl, the reaction proceeds through the formation of t-butyl carbocation

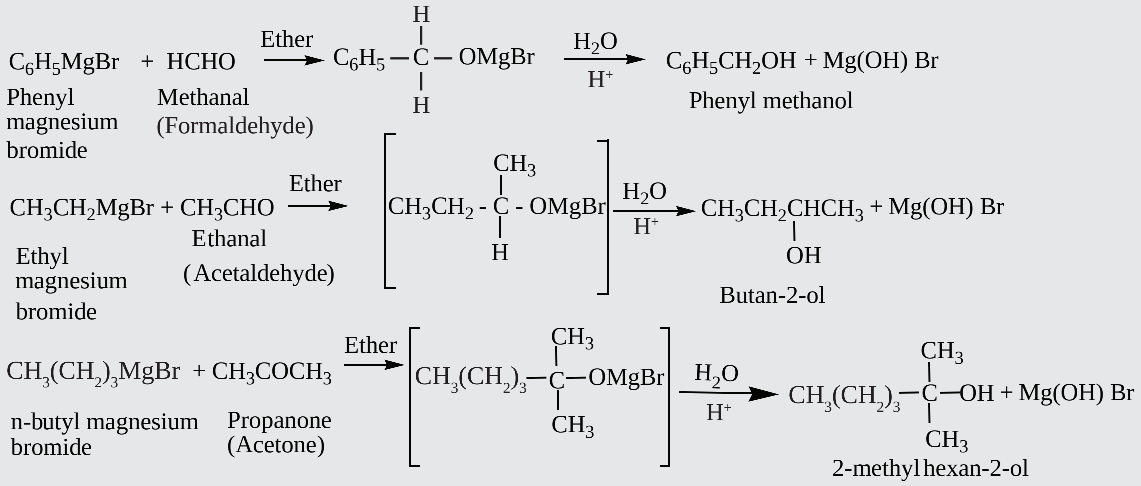
2. **From alkenes:** Addition of water across the double bond of an alkene in presence of concentrated sulphuric acid gives alcohols. This addition reaction follows Markownikoff's rule.

Example: $CH_3\text{-}CH{=}CH_2 + H_2O \xrightarrow{Conc.H_2SO_4} CH_3\text{-}CH(OH)\text{-}CH_3$

propylene propan-2-ol

3. **From Grignard reagent:** Nucleophilic addition of Grignard reagent to aldehydes/ketones in presence of dry ether followed by the acid hydrolysis gives alcohols. Formaldehyde gives primary alcohol and other aldehydes give secondary alcohols. Ketones give tertiary alcohols.

Examples



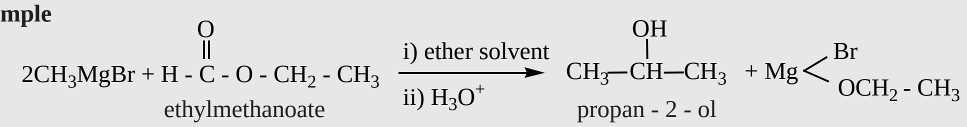
$$C_6H_5MgBr + HCHO \xrightarrow{Ether} C_6H_5-CH_2-OMgBr \xrightarrow[H^+]{H_2O} C_6H_5CH_2OH + Mg(OH)Br$$

$$CH_3CH_2MgBr + CH_3CHO \xrightarrow{Ether} \left[CH_3CH_2-CH(CH_3)-OMgBr\right] \xrightarrow[H^+]{H_2O} CH_3CH_2CH(OH)CH_3 + Mg(OH)Br$$

$$CH_3(CH_2)_3MgBr + CH_3COCH_3 \xrightarrow{Ether} \left[CH_3(CH_2)_3-C(CH_3)_2-OMgBr\right] \xrightarrow[H^+]{H_2O} CH_3(CH_2)_3-C(CH_3)_2-OH + Mg(OH)Br$$

Formate ester is used to prepare a secondary alcohol with identical alkyl groups

Example



$$2CH_3MgBr + H\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}CH_2\text{-}CH_3 \xrightarrow[ii)\ H_3O^+]{i)\ ether\ solvent} CH_3-\overset{OH}{\overset{|}{C}H}-CH_3 + Mg\begin{matrix}Br\\OCH_2-CH_3\end{matrix}$$

4. Hydroboration:

Diborane reacts with an alkene to form trialkyl borane which on treatment with H_2O_2 in presence of NaOH gives an alcohol. (Refer reactions of diborane) The overall reaction is hydration of an alkene. This reaction yields an anti-Markownikoff's product.

$$6CH_3-CH=CH_2 + B_2H_6 \longrightarrow 2(CH_3-CH_2-CH_2)_3B$$

Tripropylborane

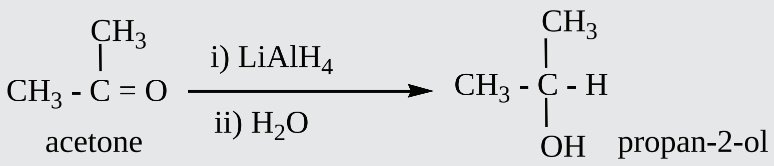
$$(CH_3-CH_2-CH_2)_3B + 3H_2O_2 \xrightarrow{OH^-} 3CH_3-CH_2-CH_2-OH + B(OH)_3$$

propan-1-ol

5. Reduction of carbonyl compounds:

Reduction of aldehydes/ketones with $LiAlH_4$ in the presence of solvents like THF (Tetrahydrofuran) followed by hydrolysis gives alcohols. Unlike other reducing agents such as Raney Ni, Na-Hg/H_2O, the lithium aluminium hydride does not reduce the carbon–carbon double bond present in unsaturated carbonyl compound and hence it is a best reagent to prepare unsaturated alcohols.

Examples



$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}}=O \xrightarrow[\text{ii) } H_2O]{\text{i) } LiAlH_4} CH_3-\underset{\displaystyle OH}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-H$$

acetone propan-2-ol

$$C_6H_5\text{-}COOH \xrightarrow[\text{(ii)}H_2O]{\text{(i)}LiAlH_4} C_6H_5CH_2OH$$

Benzoic acid Phenyl methanol(Benzyl alcohol)

$$CH_3COOCH_2CH_3 \xrightarrow[\text{(ii)}H_2O]{\text{(i)}LiAlH_4} 2CH_3CH_2OH$$

Ethyl ethanoate Ethanol

(ethyl acetate)

$$CH_3\text{-}CH=CH\text{-}CHO \xrightarrow[\text{(ii)}H_2O]{\text{(i)}LiAlH_4} CH_3\text{-}CH=CH\text{-}CH_2OH$$

crotonaldehyde crotyl alcohol

(but-2-enal) (but-2-en-1-ol)

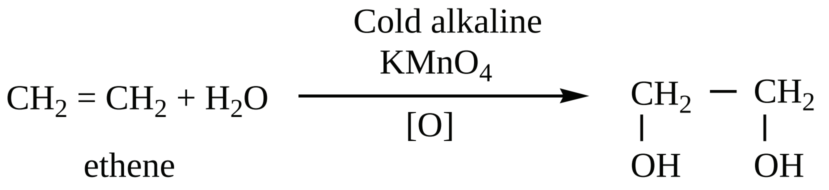
When two or more functional groups are present in a molecule a less vigorous sodium borohydride is used as a reducing agent to reduce the more reactive group. For example, if a compound contains both carbonyl and carboxyl group, it preferentially reduces the carbonyl group.

$$RCOCH_2CH_2COOH \xrightarrow[H_3O^+]{NaBH_4} RCHOH\text{-}CH_2CH_2COOH$$

4-alkyl- 4- hydroxybutanoic acid

Preparation of glycol

We have already learnt that the hydroxylation of ethylene using cold alkaline solution of potassium permanganate (Baeyer's reagent) gives ethylene glycol.

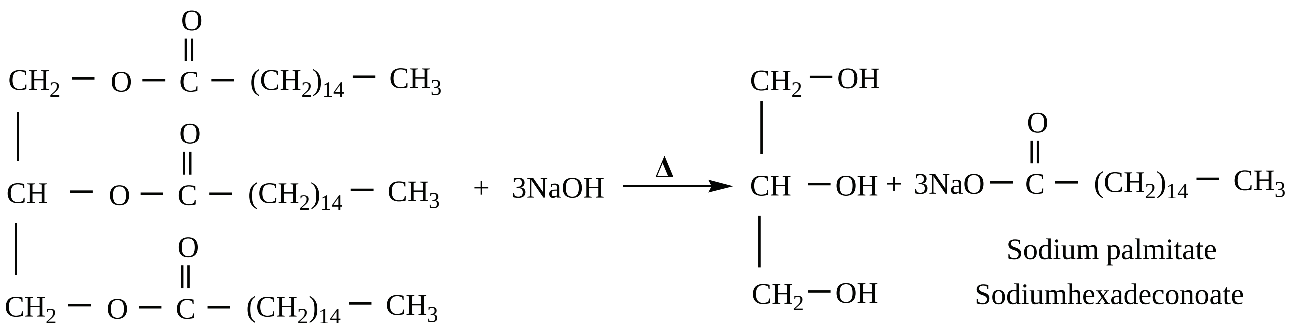


$$CH_2=CH_2+H_2O \xrightarrow[\text{[O]}]{\text{Cold alkaline } KMnO_4} \underset{OH}{CH_2}-\underset{OH}{CH_2}$$

ethane-1,2-diol

Preparation of glycerol

Glycerol occurs in many natural fats and it is also found in long chain fatty acids in the form of glyceryl esters (Triglycerides). The alkaline hydrolysis of these fats gives glycerol and the reaction is known as saponification.



Glycerylpalmitate
(a triglyceride)

Glycerol
(propane-1,2,3-triol)

Evaluate Yourself?

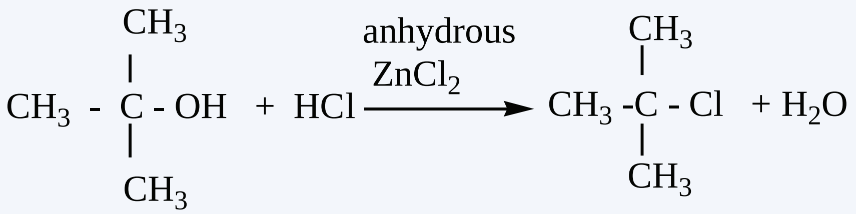
1. Suggest a suitable carbonyl compound for the preparation of pent-2-en-1-ol using $LiAlH_4$.
2. 2-methylpropene $\xrightarrow{H_2SO_4/H_2O}$?
3. How will you prepare the following using Grignard reagent.
   i) t-butyl alcohol
   ii) allyl alcohol

Methods to differentiate primary, secondary and tertiary alcohols.

The following tests are used to distinguish between 1°, 2° and 3° alcohols.

a) Lucas test:

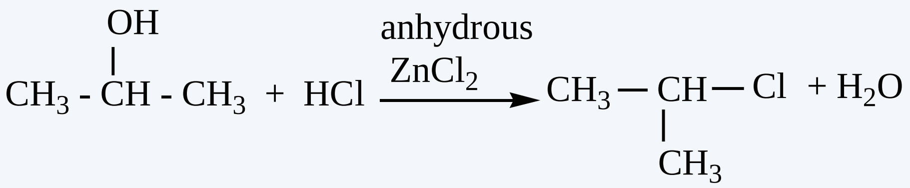
When alcohols are treated with Lucas agent (a mixture of concentrated HCl and anhydrous $ZnCl_2$) at room temperature, tertiary alcohols react immediately to form a turbidity due to the formation of alkyl chloride which is insoluble in the medium. Secondary alcohols react within 10 minutes to form a turbidity of alkyl chloride where primary alcohols do not react at room temperature.



$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-OH + HCl \xrightarrow{\text{anhydrous } ZnCl_2} CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-Cl + H_2O$$

2-methylpropan-2-ol

2 -chloro-2-methylpropane
(immediate appearance of turbidity)



$$CH_3-\overset{\displaystyle OH}{CH}-CH_3 + HCl \xrightarrow{\text{anhydrous } ZnCl_2} CH_3-\underset{\displaystyle CH_3}{CH}-Cl + H_2O$$

propan-2-ol

2 -chloropropane
(slow appearance of turbidity)

$$CH_3-CH_2-OH + HCl \xrightarrow{\text{anhydrous } ZnCl_2} \text{No reaction at room temperature}$$

ethanol

(Turbidity appears only on heating)

b) Victor Meyer's test:

This test is based on the behaviour of the different nitro alkanes formed by the three types of alcohols with nitrous acid and it consists of the following steps.

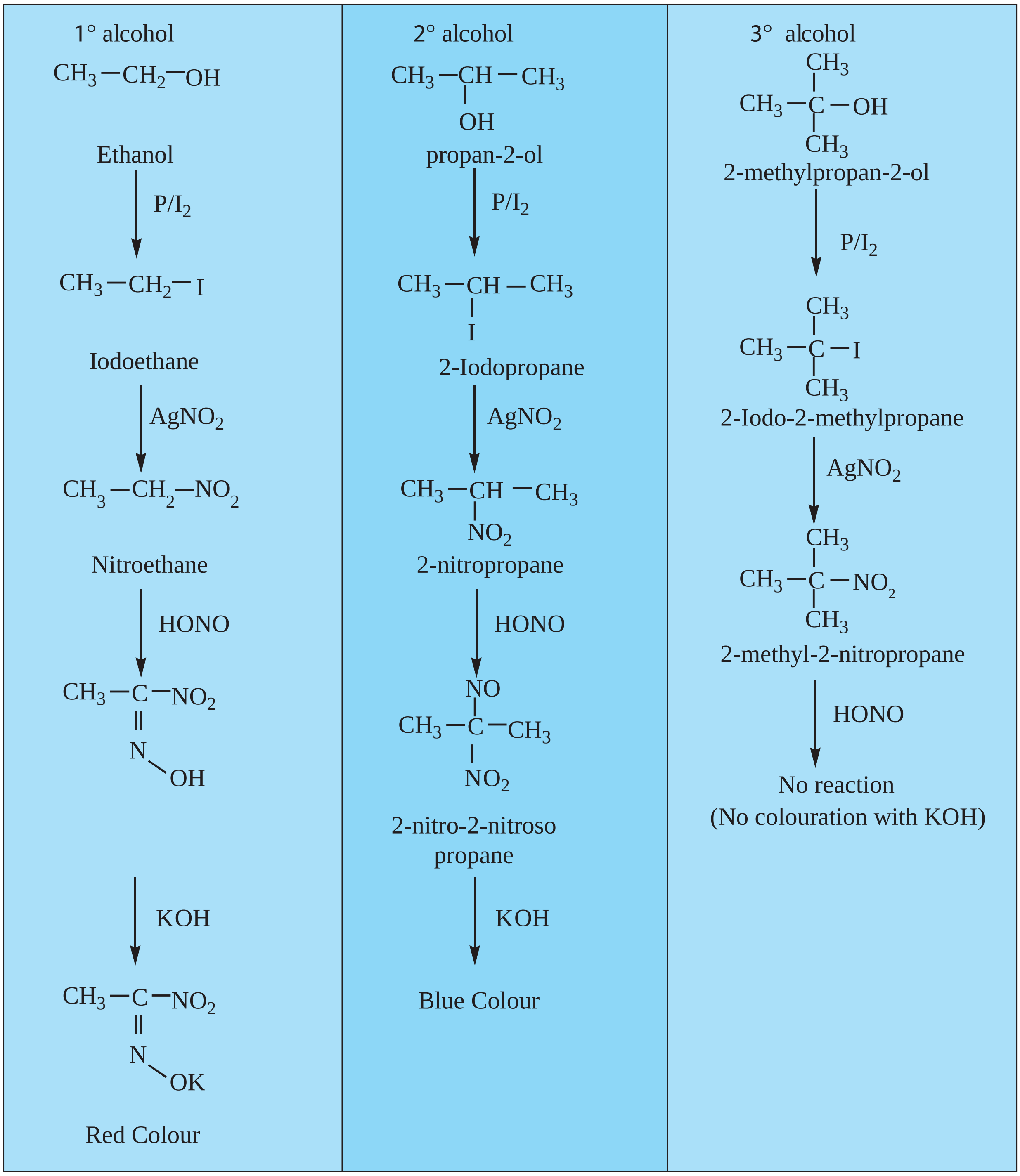
i) Alcohols are converted into alkyl iodide by treating it with I_2/P .

ii) Alkyl iodide so formed is then treated with $AgNO_2$ to form nitro alkanes.

ii) Nitro alkanes are finally treated with HNO_2 (mixture of $NaNO_2$ / HCl) and the resultant solution is made alkaline with KOH.

Result:

- Primary alcohol gives red colour
- Secondary alcohol gives blue colour.
- No colouration will be observed in case of tertiary alcohol.



Properties of alcohols

Physical properties

i. Lower alcohols are colourless liquids and the higher members are waxy solids.

ii. They have higher boiling points than the corresponding other organic compounds such as alkanes, aldehydes, ethers etc., this is due to the presence of intermolecular hydrogen bonding present in alcohols.

iii. Among isomeric alcohols primary alcohols have higher boiling point and the tertiary alcohols have lower boiling points.

iv. The lower members are highly soluble in water due to the formation of intermolecular hydrogen bonding with water.

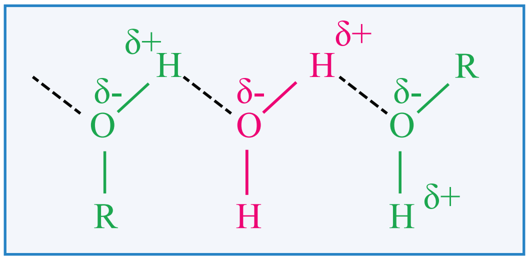


Table : Boiling point of alcohols in comparision with other organic compounds.

S.No.	Compound	Molecule formula	Molar mass	Boiling point (K)
1	Butane	CH_3-CH_2-CH_2-CH_3	58	272.5
2	Propanal	CH_3-CH_2-CHO	58	322
3	Methoxyethane	CH_3-O-CH_2-CH_3	60	283.8
4	Prapan – 1- ol	CH_3-CH_2-CH_2-OH	60	370.4
5	Propan – 2- ol	CH_3-CH(OH)-CH_3	60	355.5

Chemical properties of alcohols

Nucleophilic substitution reactions of alcohols

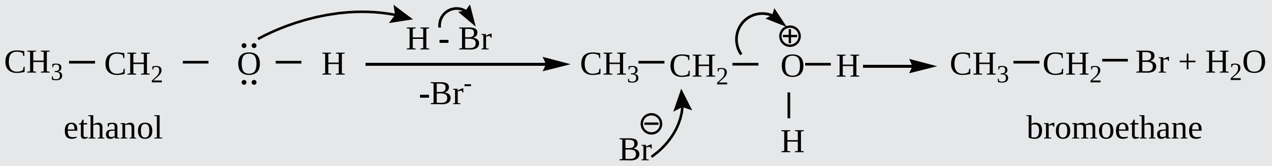
Alcohol has a strong basic leaving group (OH^-). So, –OH group is first converted into $-\overset{+}{O}H_2$ group by adding an acid. The $-\overset{+}{O}H_2$ group in the protonated alcohol can be easily displaced by a nucleophile such as Br^- to give alkyl halides.

Example: Alcohols undergo nucleophilic substitution reaction with hydro halic acids to form alkyl halides. In case of tertiary alcohols heating is required.

$$\underset{\text{Ethanol}}{CH_3-CH_2-OH} \xrightarrow[-\,H_2O]{HBr} \underset{\text{Bromoethane}}{CH_3-CH_2-Br}$$

Alkyl halide formation from primary alcohols follow S_N2 mechanism

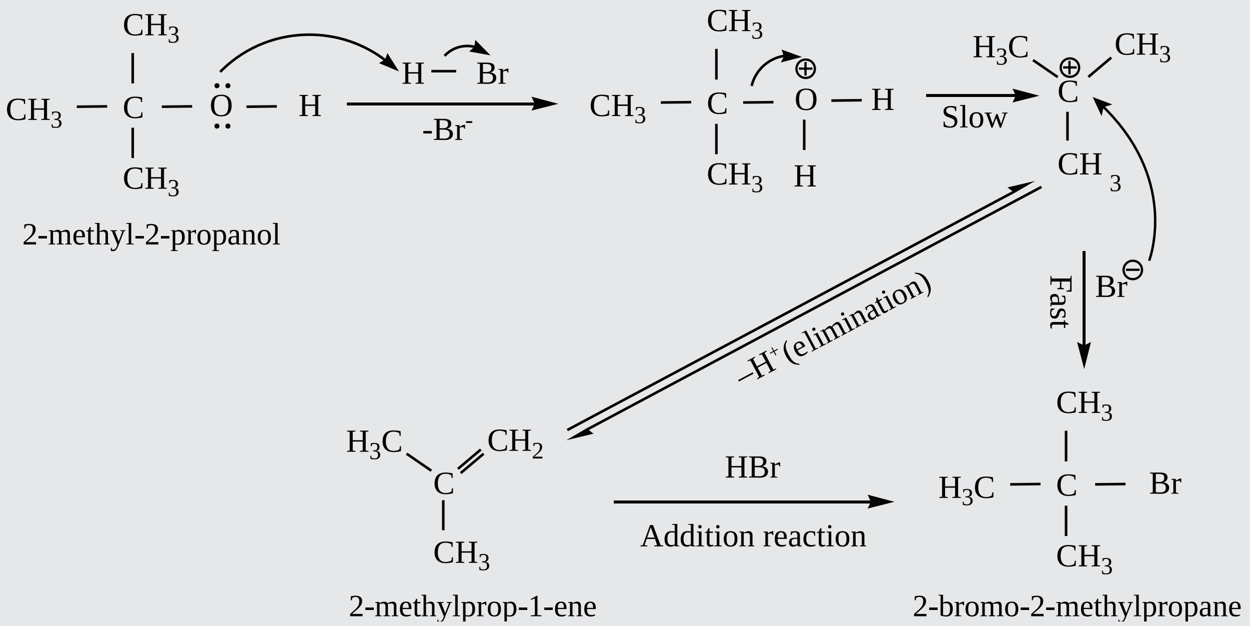
Example



Nucleophilic attack of Br^- and leaving of H_2O takes place simultaneously.

Alkyl halide formation of tertiary alcohols follow S_N1 mechanism.

Example



Here, the carbocation formed can undergo elimination to give an alkene. However the alkene can again undergo addition reaction with HBr to give the substituted product.

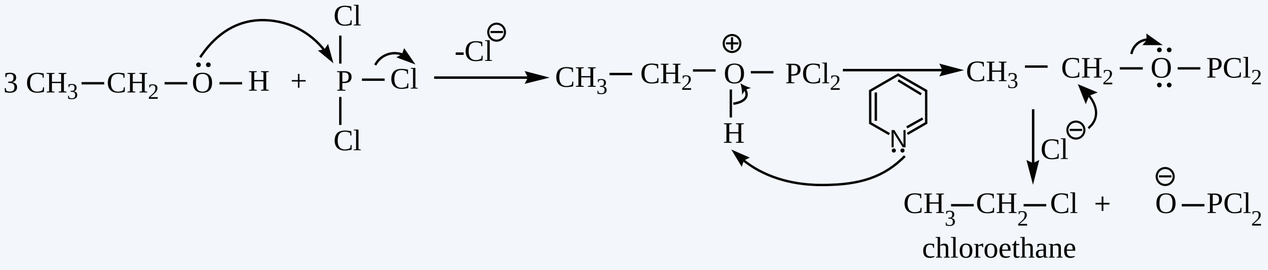
Conversion of alcohol into alkyl halides: Other methods

Alcohols can also be converted into an alkyl halides using PCl_3, PBr_3.

$$CH_3CH_2OH \xrightarrow[\text{pyridine}]{PCl_3} CH_3CH_2Cl$$

ethanol → chloroethane

Mechanism : S_N2 reaction on phosphorous tri chloride



The conversion of an alcohol to alkyl halide can also be effected using thionyl chloride

$$CH_3-OH + SOCl_2 \xrightarrow{\text{Pyridine}} CH_3-Cl + HCl + SO_2$$

Methanol, Thionyl chloride → chloromethane

This reaction also follows the S_Ni mechanism in the presence of pyridine.

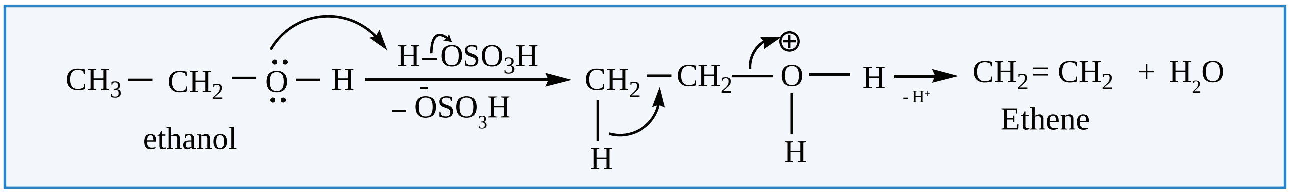
2. Elimination reactions of alcohols

When alcohols are heated with a suitable dehydrating agents like sulphuric acid, the H and OH present in the adjacent carbons of alcohols are lost, and it results in the formation of a carbon – carbon double bond. Phosphoric acid, anhydrous $ZnCl_2$, alumina etc., can also be used as dehydrating agents.

Example $CH_3-CH_2-OH \xrightarrow[443\ K]{H_2SO_4} CH_2 = CH_2 + H_2O$

Mechanism

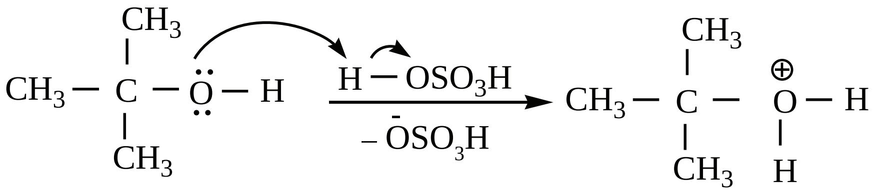
Primary alcohols undergo dehydration by E_2 mechanism



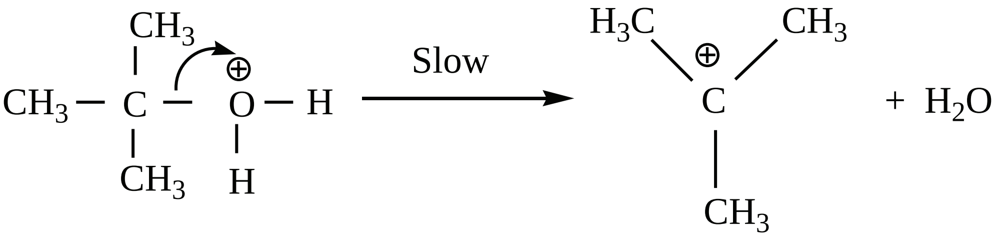
Tertiary alcohols undergo dehydration by E_1 mechanism. It involves the formation of a carbocation.

Protonation of alcohol

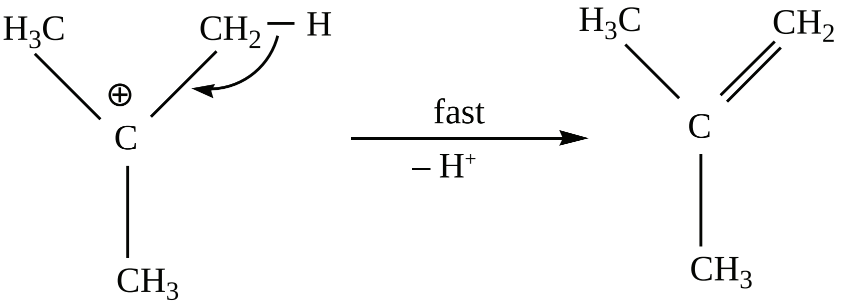
Step 1 :



Step 2 : Dissociation of oxonium ion to form a carbocation.



Step 3 : Deprotonation of carbocation to form an alkene



2 - methylprop - 1- ene

Order of reactivity:

The relative reactivities of alcohols in the dehydration reaction follows the order

primary < secondary < tertiary

Evaluate yourself

Identify the products in the following reactions. Write their IUPAC names and mention the mechanism involved in the reactions.

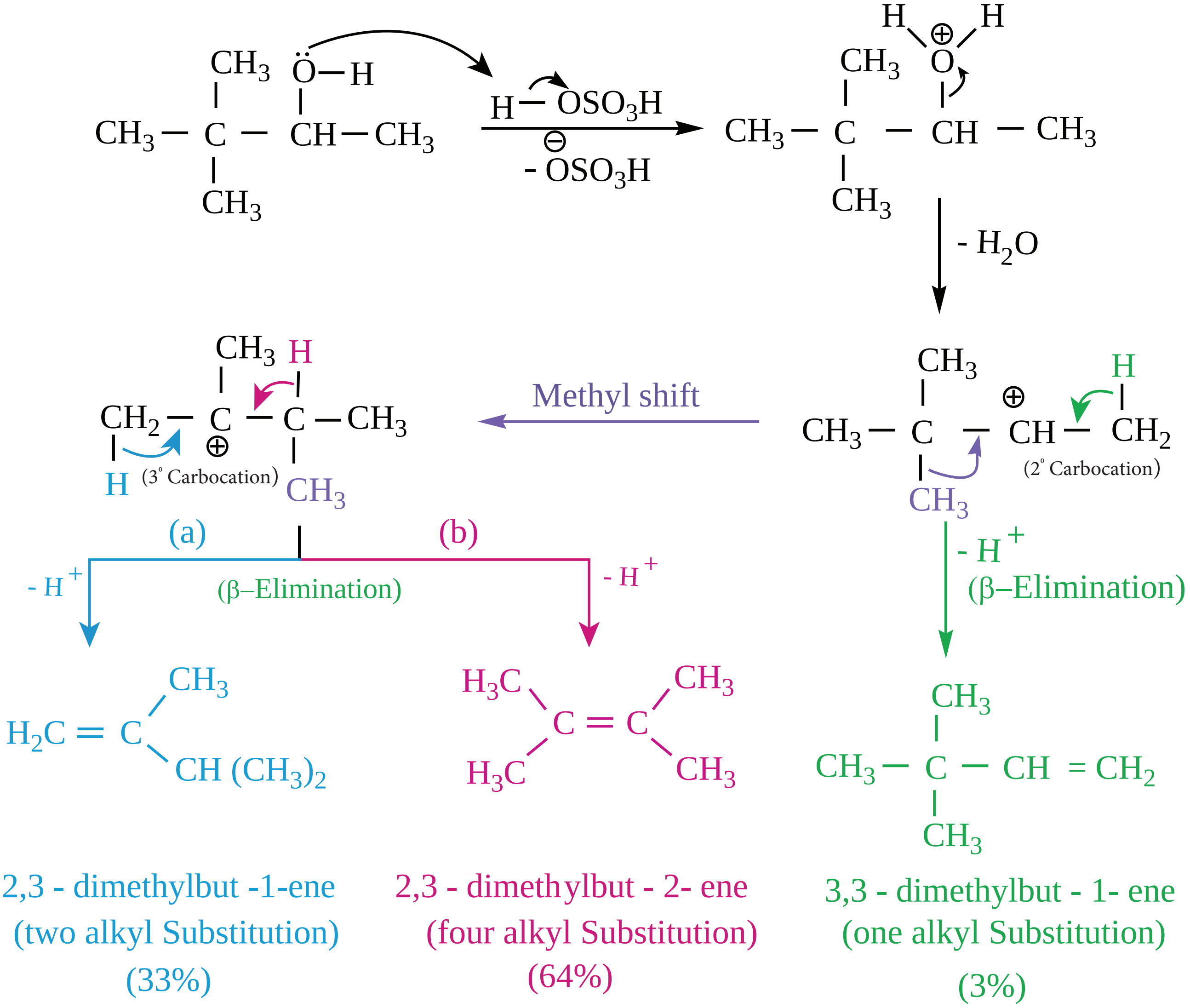
i) cyclopentanol $\xrightarrow[\Delta]{H_2SO_4}$?   ii) butan–1–ol $\xrightarrow[H_2SO_4]{NaBr}$?

iii) neopentyl alcohol $\xrightarrow{PCl_5}$?

Saytzeff's rule

During intramolecular dehydration, if there is a possibility to form a carbon – carbon double bond at different locations, the preferred location is the one that gives the more (highly) substituted alkene i.e., the stable alkene.

For example, the dehydration of 3,3 – dimethyl – 2- butanol gives a mixture of alkenes. The secondary carbocation formed in this reaction undergoes rearrangement to form a more stable tertiary carbocation.



Evaluate yourself : What is the major product obtained when 2,3 – dimethyl pentan -3 – ol is heated in the presence of H_2SO_4.

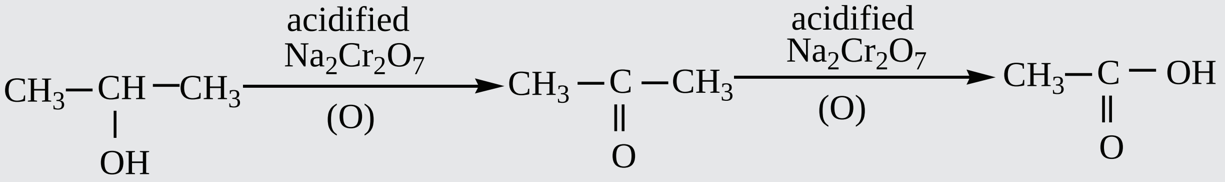
Oxidation of alcohols

The important reactions of alcohols are their oxidation to give carbonyl compounds. The commonly used oxidising agent is acidified sodiumdichromate. Oxidation of primary alcohols give an aldehyde which on further oxidation gives the carboxylic acids. To stop the oxidation reaction at the aldehyde / ketone stage, pyridinium chlorochromate (PCC) is used as an oxidising agent.

Example

$$CH_3-CH_2-OH \xrightarrow[(O)]{\text{acidified } Na_2Cr_2O_7} CH_3-CHO \xrightarrow[(O)]{\text{acidified } Na_2Cr_2O_7} CH_3-COOH$$

ethanol ethanal ethanoicacid



$$\underset{\displaystyle OH}{CH_3-\underset{|}{C}H-CH_3} \xrightarrow[(O)]{\text{acidified } Na_2Cr_2O_7} CH_3-\underset{\underset{\displaystyle O}{\|}}{C}-CH_3 \xrightarrow[(O)]{\text{acidified } Na_2Cr_2O_7} CH_3-\underset{\underset{\displaystyle O}{\|}}{C}-OH$$

Propan - 2- ol Propanone ethanoicacid

$$CH_3-CH_2-CH_2-OH \xrightarrow{PCC} CH_3-CH_2-CHO$$

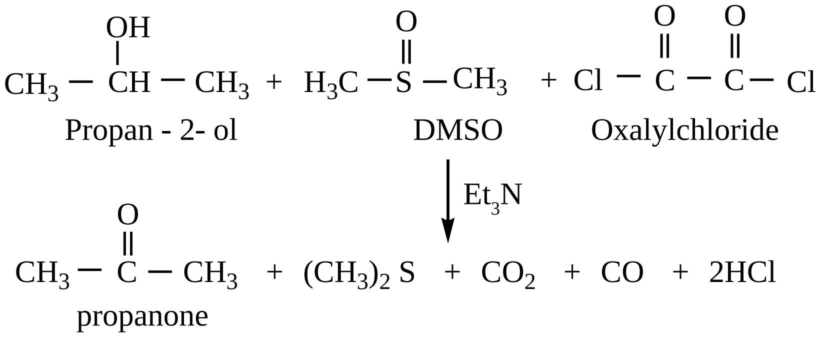
Propan - 1- ol Propanal

Tertiary alcohols do not undergo oxidation reaction under normal conditions, but at elevated temperatures, under strong oxidising agent cleavage of C –C bond takes place to give a mixture of carboxylic acid.

Swern oxidation

In this method, dimethyl sulfoxide (DMSO) is used as the oxidising agent, which converts alcohols to ketones / aldehydes.

In this method an alcohol is treated with DMSO and oxalyl chloride followed by the addition of triethylamine.



$$CH_3-\overset{\overset{\displaystyle OH}{|}}{C}H-CH_3 + H_3C-\overset{\overset{\displaystyle O}{\|}}{S}-CH_3 + Cl-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle O}{\|}}{C}-Cl \xrightarrow{Et_3N} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + (CH_3)_2S + CO_2 + CO + 2HCl$$

Propan - 2- ol DMSO Oxalylchloride

propanone

Biological oxidation

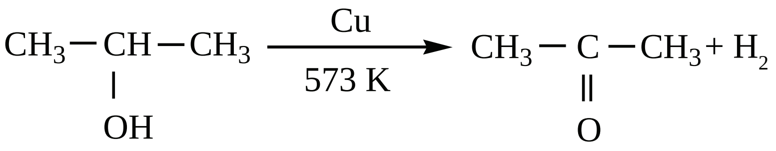
The fermentation of the food consumed by an animal produces alcohol. To detoxify the alcohol, the liver produces an enzyme called alcohol dehydrogenase (ADH). Nicotinamide adenine dinucleotide (NAD) present in the animals act as an oxidising agent and ADH catalyses the oxidation of toxic alcohols into non-toxic aldehyde.

$$\underset{\text{ethanol}}{CH_3CH_2OH} + NAD^+ \xrightarrow{ADH} \underset{\text{ethanal}}{CH_3CHO} + NADH + H^+$$

Catalytic dehydrogenation

When the vapours of a primary or a secondary alcohol are passed over heated copper at 573K, dehydrogenation takes place to form aldehyde or ketone.

$$\underset{\text{ethanol}}{CH_3 - CH_2 - OH} \xrightarrow[573\ K]{Cu} \underset{\text{ethanal}}{CH_3 - CHO} + H_2$$

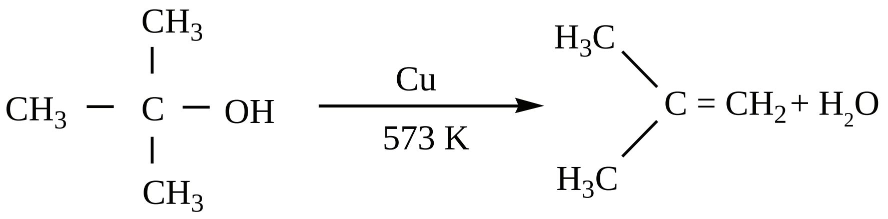


$$\underset{\text{Propan - 2- ol}}{CH_3-\underset{\underset{OH}{|}}{CH}-CH_3} \xrightarrow[573\ K]{Cu} \underset{\text{propanone}}{CH_3-\underset{\underset{O}{\|}}{C}-CH_3} + H_2$$

Propan - 2- ol

propanone

Tertiary alcohols undergo dehydration reaction to give alkenes.



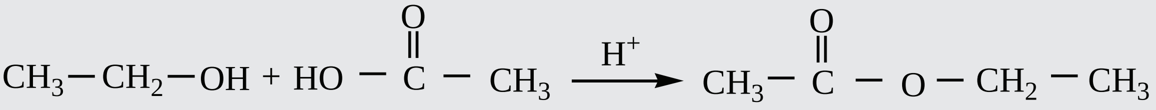
2 - methylpropan - 2- ol

2 - methylprop - 1- ene

Esterification

Alcohols react with carboxylic acids in the presence of an acid to give esters

Example



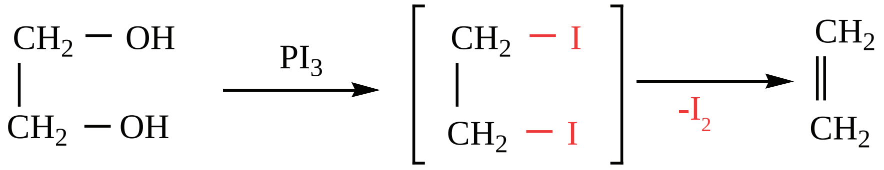
$$\underset{\text{ethanol}}{CH_3-CH_2-OH} + \underset{\text{ethanoicacid}}{HO-\overset{\overset{O}{\|}}{C}-CH_3} \xrightarrow{H^+} \underset{\text{ethylethanoate}}{CH_3-\overset{\overset{O}{\|}}{C}-O-CH_2-CH_3}$$

ethanol ethanoicacid ethylethanoate

Reactions of Glycol

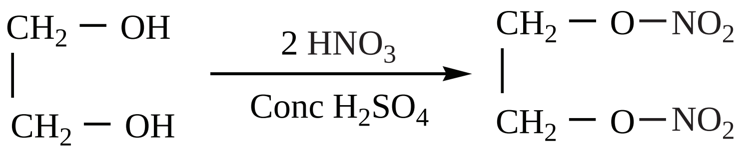
Ethylene glycol contains two primary alcoholic groups and it exhibits the usual reactions of hydroxyl group. Like other primary alcohols, it reacts with metallic sodium to form monosodium glycolate and disodium glycolate. The hydroxyl groups can be converted to the halide groups by treating glycol with halic acid (or with PCl_5 / PCl_3 / $SOCl_2$.)

When ethylene glycol is treated with HI or P/I₂, 1,2 – diiodoethane is first formed which decomposes to give ethene.



ethane - 1,2 - diol 1,2 - diiodoethane ethene

On heating with conc HNO₃ in the presence of Con. H_2SO_4, ethylene glycol forms dinitroglycol.

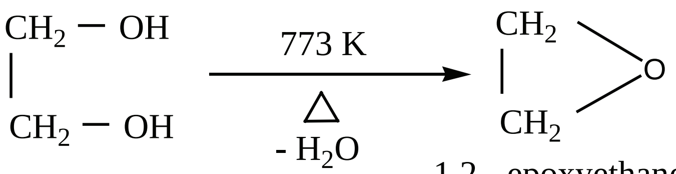


ethane - 1,2 - diol 1,2 - dinitroxyethene (dinitroglycol)

Dehydration reaction

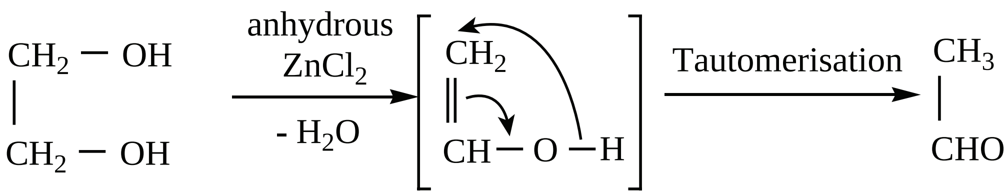
Ethyleneglycol undergoes dehydration reaction under different conditions to form different products.

1. When heated to 773K, it forms epoxides.



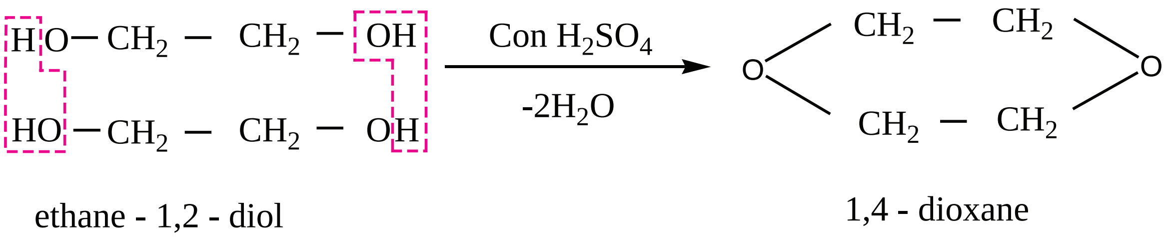
ethane - 1,2 - diol 1,2 - epoxyethane (Oxirane)

2. When heated with dilute sulphuric acid (or) anhydrous $ZnCl_2$ under pressure in a sealed tube, it gives acetaldehyde.



ethane -1,2 - diol ethenol (Vinylalcohol) Ethanal

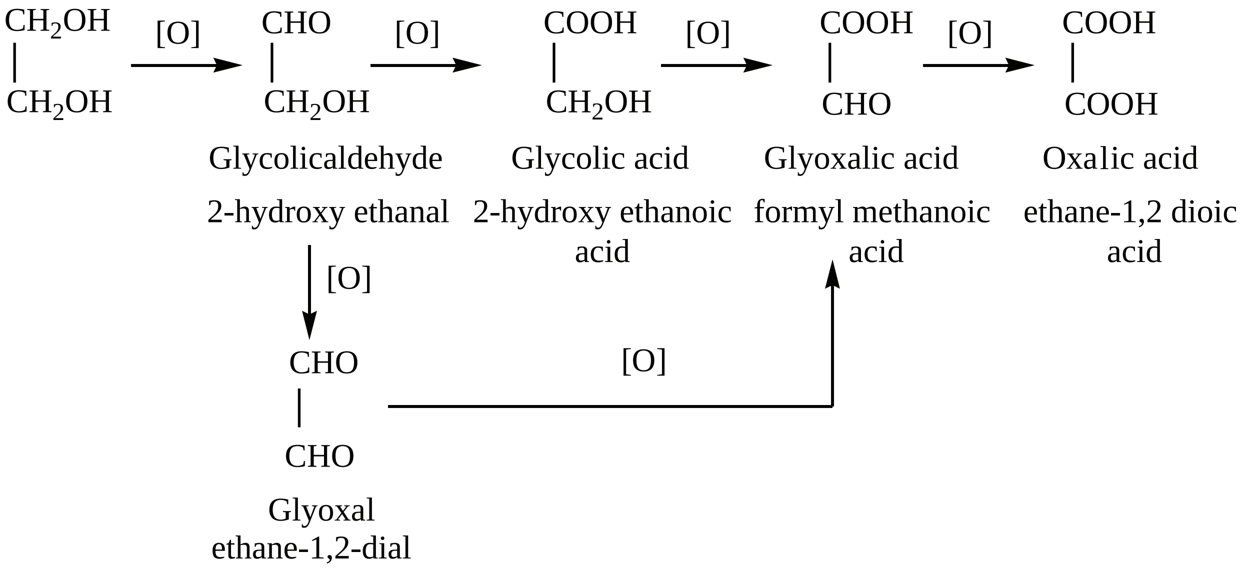
3. When distilled with Conc. H_2SO_4, glycol forms dioxane



Oxidation of glycol

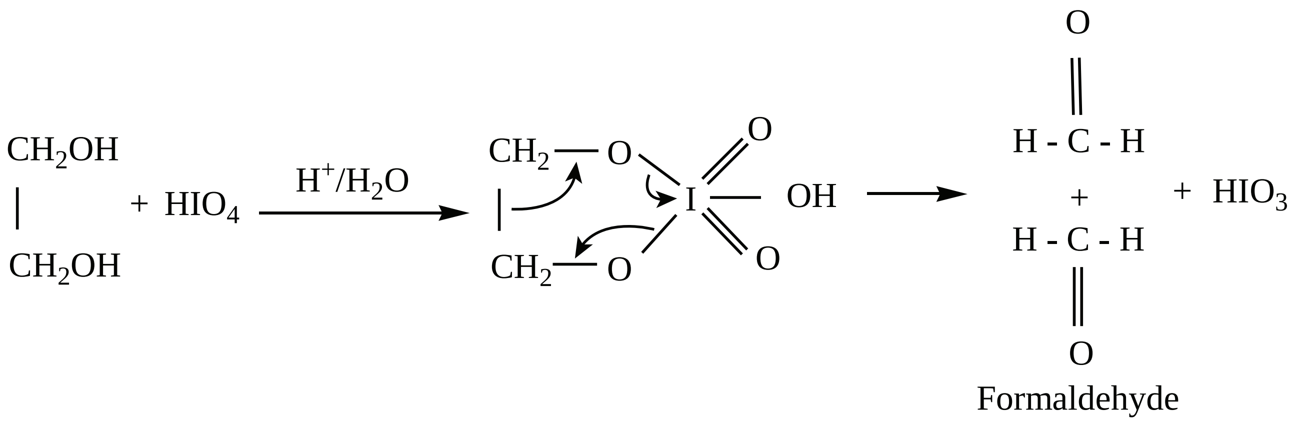
On oxidation, glycol gives a variety of products depending on the nature of oxidizing agent and other reaction conditions.

i) When nitric acid (or) alkaline potassium permanganate is used as the oxidizing agent, the following products are obtained.



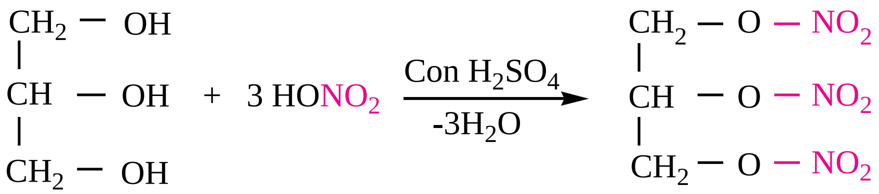
ii) **Oxidation of glycol with periodic acid**

Ethylene glycol on treatment with periodic acid gives formaldehyde. This reaction is selective for vicinal 1,2 – diols and it proceeds through a cyclic periodate ester intermediate.



Reaction of Glycerol

Nitration: Glycerol reacts with concentrated nitric acid in the presence of concentrated sulphuric acid to form TNG (nitroglycerine).



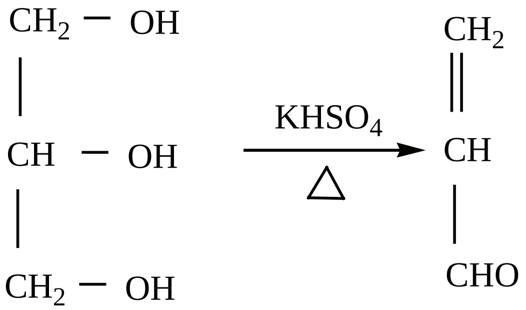
$$CH_2(OH)-CH(OH)-CH_2(OH) + 3\,HONO_2 \xrightarrow[-3H_2O]{Con\ H_2SO_4} CH_2(O-NO_2)-CH(O-NO_2)-CH_2(O-NO_2)$$

Propan - 1,2,3 - triol
glycerol

1,2,3 - trinitroxy propane

Dehydration

When glycerol is heated with dehydrating agents such as Con H_2SO_4,$KHSO_4$ etc…., it undergoes dehydration to form acrolein.



$$CH_2(OH)-CH(OH)-CH_2(OH) \xrightarrow[\triangle]{KHSO_4} CH_2=CH-CHO$$

Propane - 1,2,3 - triol

Prop - 2- enal (acrolein)

Oxidation

Glycerol can give rise to a variety of oxidation products depending on the nature of the oxidising agent used for oxidation.

a) Oxidation of glycerol with dil. HNO_3 gives glyceric acid and tartronic acid.

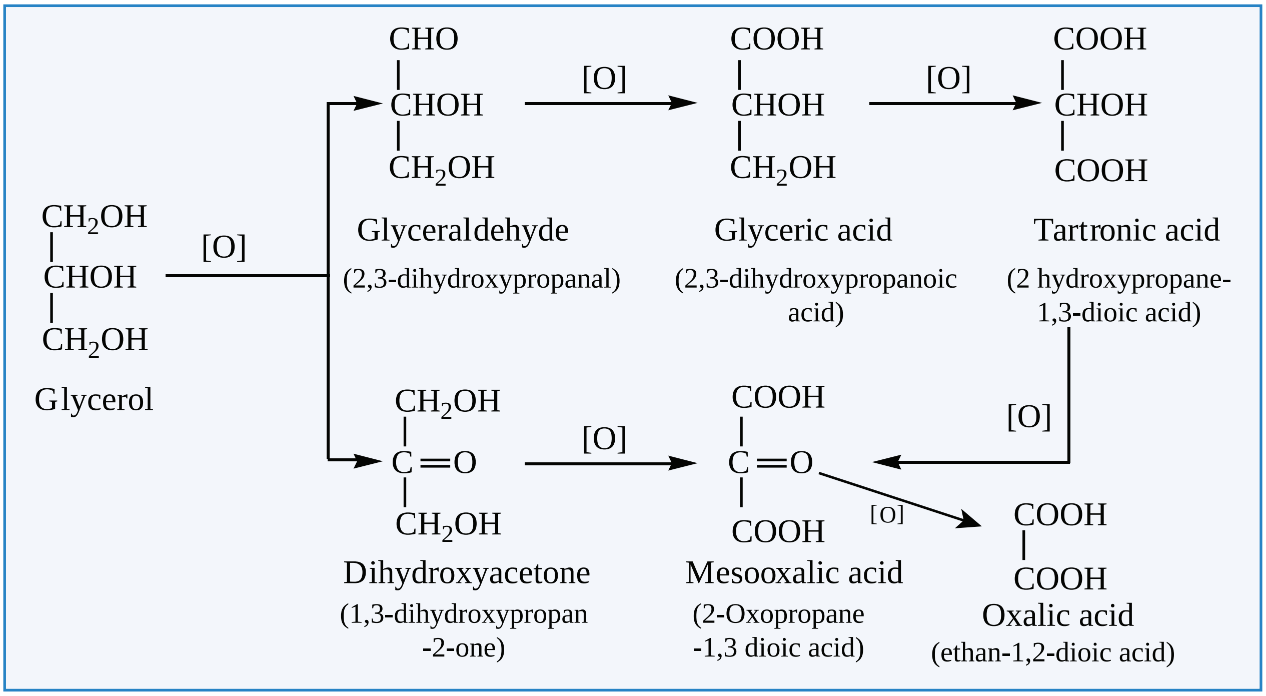
b) Oxidation of glycerol with Conc. HNO_3 gives mainly glyceric acid.

c) Oxidation of glycerol with bismuth nitrate gives as meso oxalic acid.

d) Oxidation of glycerol with Br_2/H_2O (or) NaOBr (or) Fenton's reagent ($FeSO_4 + H_2O_2$) gives a mixture of glyceraldehyde and dihydroxy acetone(This mixture is named as glycerose).

e) On oxidation with HIO_4 or Lead tetra acetate (LTA) it gives formaldehyde and formic acid.

f) Acidified $KMnO_4$ oxidises glycerol into oxalicacid.



Uses of alcohols

Uses of methanol :

1. Methanol is used as a solvent for paints, varnishes, shellac, gums, cement, etc.
2. In the manufacture of dyes, drugs, perfumes and formaldehyde.

Uses of ethanol:

1. It is also used in the preparation of
    a) Paints and varnishes.
    b) Organic compounds like ether, chloroform, iodoform, etc.,
    c) Dyes, transparent soaps.
2. As a substitute for petrol under the name power alcohol used as fuel for aeroplane
3. It is used as a preservative for biological specimens.

Uses of ethylene glycol:

1. Ethylene glycol is used as an antifreeze in automobile radiator
2. Its dinitrate is used as an explosive with TNG.

Uses of glycerol

1. Glycerol is used as a sweetening agent in confectionary and beverages.
2. It is used in the manufacture of cosmetics and transparent soaps.
3. It is used in making printing inks and stamp pad ink and lubricant for watches and clocks.
4. It is used in the manufacture of explosive like dynamite and cordite by mixing it with china clay

Acidity of alcohols

According to Bronsted theory, an acid is defined as a proton donor and the acid strength is the tendency to give up a proton. Alcohols are weakly acidic and their acidity is comparable with water. Except methanol, all other alcohols are weaker acid than water. The K_a value for water is 1.8×10^{-16} where as for alcohols, the K_a value in the order 10^{-18} to 10^{-16}.

Alcohols react with active metals such as sodium, aluminium etc… to form the corresponding alkoxides with the liberation of hydrogen gas and similar reaction to give alkoxide is not observed in the reaction of alcohol with NaOH.

$$2C_2H_5\text{-}OH + 2Na \rightarrow 2C_2H_5ONa + H_2\uparrow$$

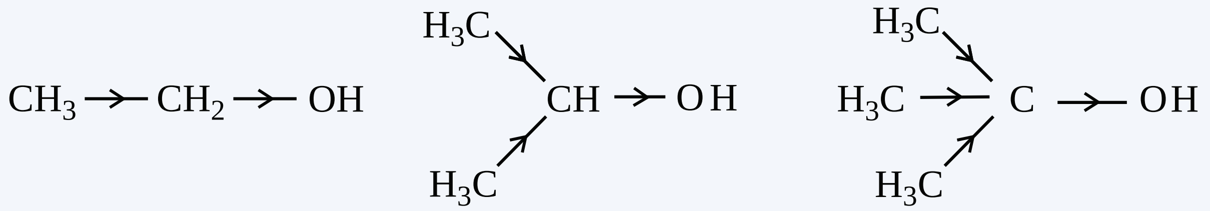
The above reaction explains the acidic nature of alcohols.

Comparison of acidity of 1°, 2°and 3° alcohols

The acidic nature of the alcohol is due to the polar nature of O –H bond. When an electron withdrawing -I groups such as -Cl, - F etc… is attached to the carbon bearing the OH group, it withdraws the electron density towards itself and thereby facilitating the proton donation. In contrast, the electron releasing group such as alkyl group increases the electron density on oxygen and decreases the polar nature of O – H bond, Hence it results in the decrease in acidity. on moving from primary to secondary and tertiary alcohols, the number of alkyl groups which attached to the carbon bearing -OH group increases, which results in the following order of acidity.

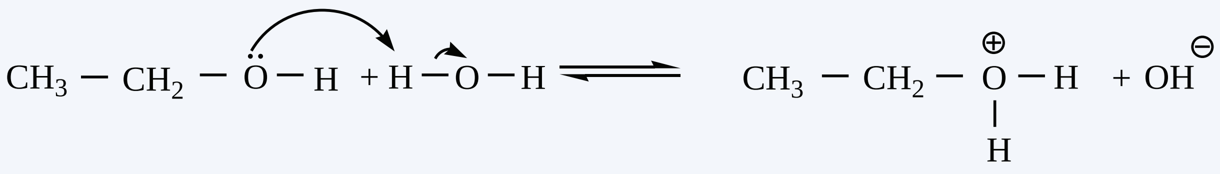
1° alcohol > 2° alcohol > 3° alcohol

For example



$K_a = 1.3\times10^{-16}$ $K_a = 3.2\times10^{-17}$ $K_a = 1\times10^{-18}$

Alcohols can also act as a Bronsted bases. It is due to the presence of unshared electron pairs on oxygen which make them proton acceptors.



$$CH_3-CH_2-\ddot{O}-H + H-O-H \rightleftharpoons CH_3-CH_2-\overset{\oplus}{\underset{\substack{|\\H}}{O}}-H + \overset{\ominus}{OH}$$

Acidity of Phenol

Phenol is more acidic than aliphatic alcohols. Unlike alcohols it reacts with bases like sodium hydroxide to form sodium phenoxide. This explains the acidic behaviour of phenol.let us consider the aqueous solution of phenol in which the following equilibrium exists.

$$C_6H_5 - OH + H.OH \rightleftharpoons C_6H_5 - \overset{\ominus}{O} + H_3O^{\oplus}$$

K_a value for the above equilibrium is 1×10^{-10} at $25^{\circ}C$. This Ka value indicates that it is more acidic than aliphatic alcohols. This increased acidic behaviour can be explained on the basis of the stability of phenoxide ion. We have already learnt in XI standard that the phenoxide is more stabilised by resonance than phenol.

In substituted phenols, the electron withdrawing groups such as $-NO_2$,$-Cl$ enhances the acidic nature of phenol especially when they are present at ortho and para positions. In such cases,there is a possibility for the extended delocalisation of negative charge on the phenoxide ion. On the other hand the alkyl substitued phenols show a decreased acidity due to the electron releasing +I effect of alkyl group.

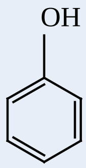
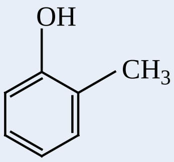
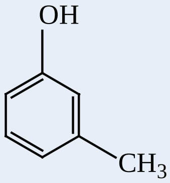
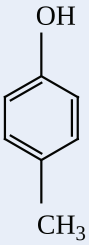
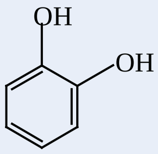
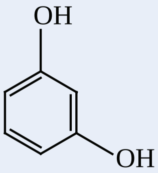
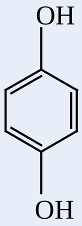
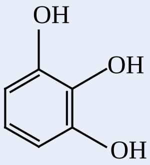
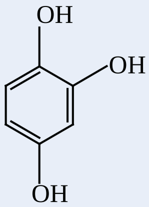
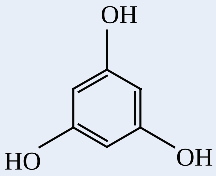
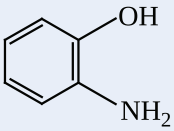
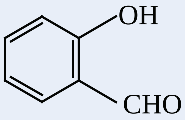
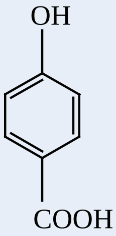
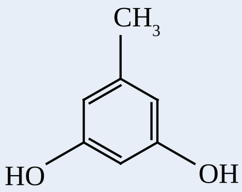
Table: pK_a Values of some alcohols and phenols

S.No.	Compound	pK_a Value
1	methanol	15.5
2	ethanol	15.9
3	propan – 2- ol	16.5
4	2 – methyl propan 2 - ol	18.0
5	Cyclohexanol	18.0
6	Phenol	10.0
7	o – nitrophenol	7.2
8	p – nitrophenol	7.1
9	m - nitrophenol	8.3
10	o – cresol	10.2
11	m – cresol	10.1
12	p – cresol	10.2

Phenols:

Phenols are organic compounds in which a -OH group is directly attached to a benzene ring. The carbon bearing the -OH group is sp^2 hybridized.

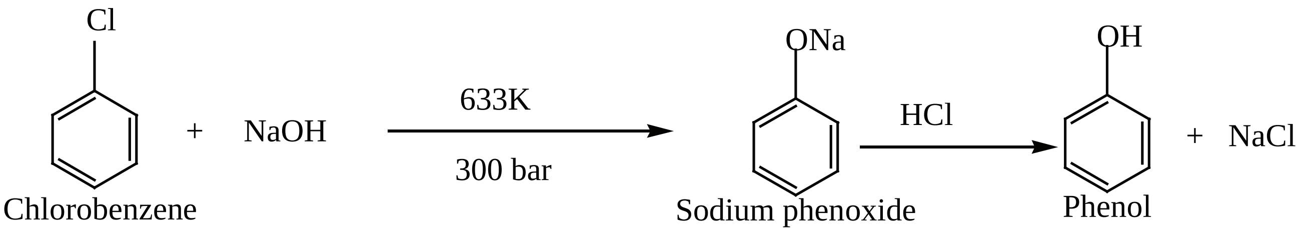
Table: Classification of phenols

Monohydric Phenol	Monohydric phenols				
					
	Common Name:	Phenol	o -cresol	m-cresol	p-cresol
	IUPAC Name :	Phenol	2-methyl phenol	3-methyl phenol	4-methyl phenol
Dihydric Phenol	Dihydric phenols				
					
	Common Name:	Catechol	Resorcinol	Quinol	
	IUPAC Name:	1,2- dihydroxybenzene	1,3-dihydroxybenzene	1,4-dihydroxybenzene	
Trihydric Phenol	Trihydric phenols				
					
	Common Name:	Pyrogallol	Hydroxyquinol	Phloroglucinol	
	IUPAC Name:	1,2,3-trihydroxybenzene	1,2,4-trihydroxybenzene	1,3,5-trihydroxybenzene	
Substituted phenol	Substituted phenols				
					
		o-amino phenol	o-hydroxy Benzaldehyde	p-hydroxy benzoic acid	Orcinol(or) 3,5-Dihydroxy toluene

Preparation of Phenols

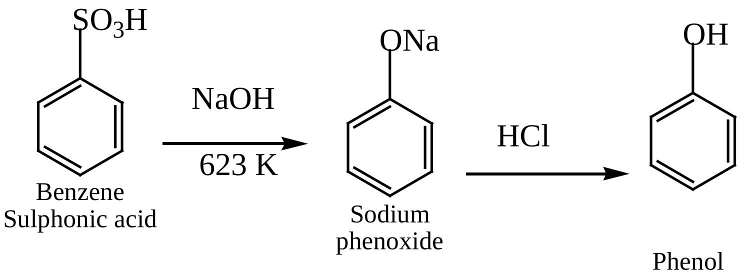
a) From halo arenes(Dows process)

When Chlorobenzene is hydrolysed with 6-8% NaOH at 300 bar and 633K in a closed vessel,sodium phenoxide is formed which on treatment with dilute HCl gives phenol.



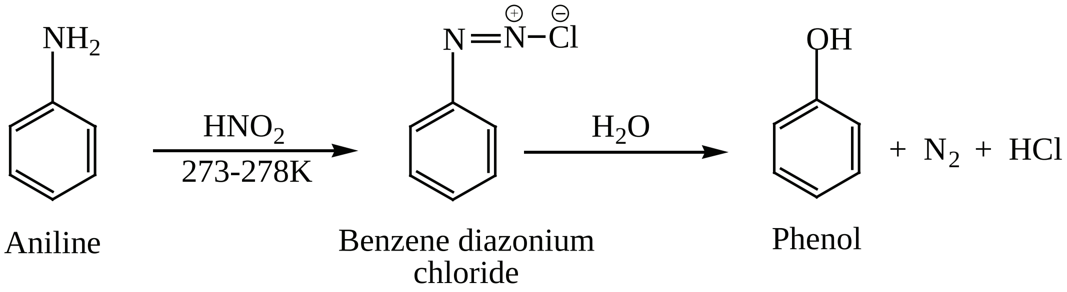
b) From benzene sulphonic acid

Benzene is sulphonated with oleum and the benzene sulphonic acid so formed is heated with molten NaOH at 623K gives sodium phenoxide which on acidification gives phenol.



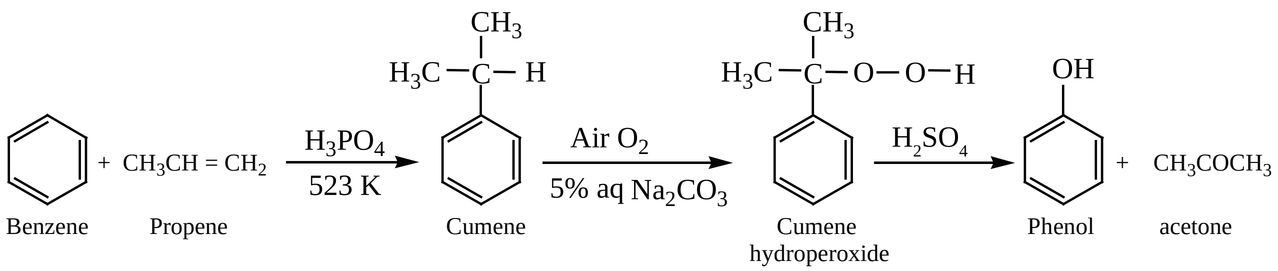
c) From aniline

Aniline is diazotized with nitrous acid $(NaNO_2+HCl)$ at 273-278K to give benzene diazonium chloride which on further treatment with hot water in the presence of mineral acid gives phenol.



d) From cumene

A mixture of benzene and propene is heated at 523K in a closed vessel in presence of H_3PO_4 catalyst gives cumene (isopropylbenzene). On passing air to a mixture of cumene and 5% aqueous sodium carbonate solution, cumene hydro peroxide is formed by oxidation. It is treated with dilute acid to get phenol and acetone. Acetone is also an important byproduct in this reaction.



Physical Properties

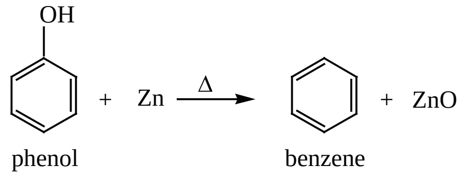
Phenol is colourless, needle shaped crystal, hygroscopic, corrosive and poisonous. It turns pink on exposure to air and light. The simplest phenols are liquids or low melting solids, they have quite high boiling points. Phenol is slightly soluble in water because of hydrogen bonding. However other substituted phenols are essentially insoluble in water.

Chemical Properties:

Reactions involving -OH group.

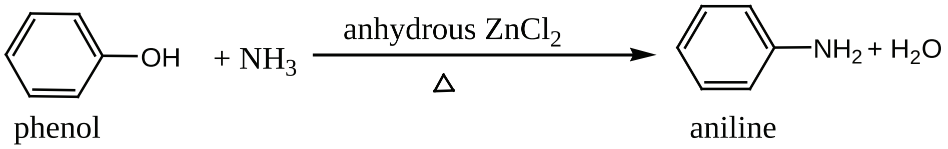
a) Reaction with Zn dust:

Phenol is converted to benzene on heating with zinc dust. In this reaction the hydroxyl group which is attached to the aromatic ring is eliminated.



b) Reaction with ammonia:

Phenol on heating with ammonia in presence of anhydrous $ZnCl_2$ gives aniline.



c) Formation of esters:

Schotten-Baumann reaction :

Phenol on treatment with acid chlorides gives esters. The acetylation and benzoylation of phenol are called Schotten-Baumann reaction.

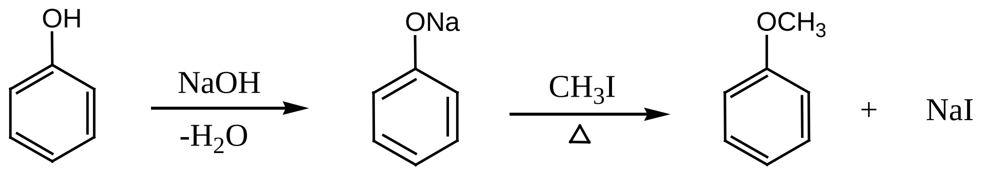
$$\underset{\text{phenol}}{C_6H_5OH} + \underset{\text{acetyl chloride}}{CH_3COCl} \xrightarrow[\text{Py}]{\text{NaOH}} \underset{\text{phenyl ethanoate}}{CH_3\text{-}COOC_6H_5} + HCl$$

$$\underset{\text{phenol}}{C_6H_5OH} + \underset{\text{benzoyl chloride}}{C_6H_5COCl} \xrightarrow[\text{Py}]{\text{NaOH}} \underset{\text{phenyl benzoate}}{C_6H_5\text{-}COOC_6H_5} + HCl$$

d) Formation of ethers:

Williamson ether synthesis:

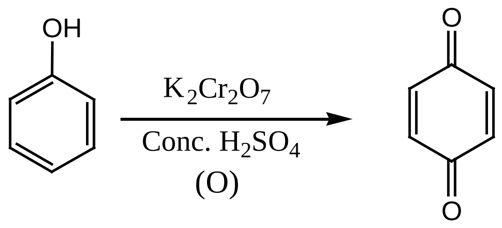
An alkaline solution of phenol reacts with alkyl halide to form phenyl ethers. The alkyl halide undergoes nucleophilic substitution by the phenoxide ion in the presence of alkali.



Phenol Sodium Phenoxide Anisole (methoxybenzene)

d) Oxidation:

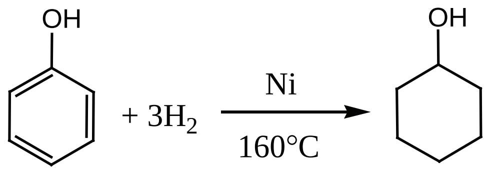
Phenol undergoes oxidation with air or acidified $K_2Cr_2O_7$ with conc. H_2SO_4 to form 1,4-benzoquinone.



Phenol 1,4-benzoquinone

e) Reduction:

Phenol on catalytic hydrogenation gives cyclohexanol.



Phenol cyclohexanol

Reactions of benzene ring:

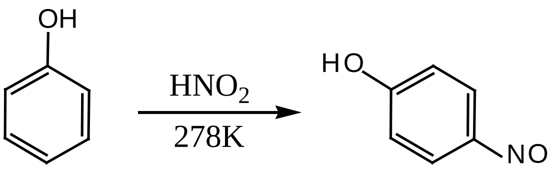
Electrophilic aromatic substitution:

We have already learnt in XI standard that the groups like $-\ddot{O}H$, $-\ddot{N}H_2$, etc., which when directly attached to the benzene ring, activate the ring towards electrophilic substitution reaction and direct the incoming electrophile to occupy either the ortho or para position.

Common electrophilic aromatic substitutions are as follows:

i) Nitrosation:

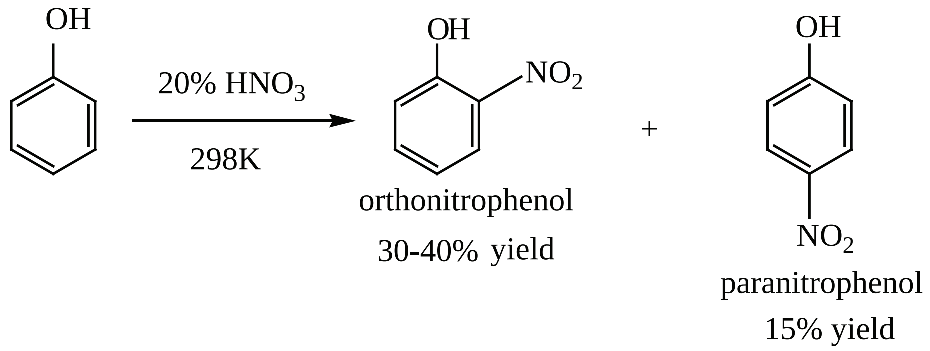
Phenol can be readily nitrosoated at low temperature with HNO_2.



phenol p-nitroso phenol

ii) Nitration:

Phenol can be nitrated using 20% nitric acid even at room temperature, a mixture of ortho and para nitro phenols are formed.

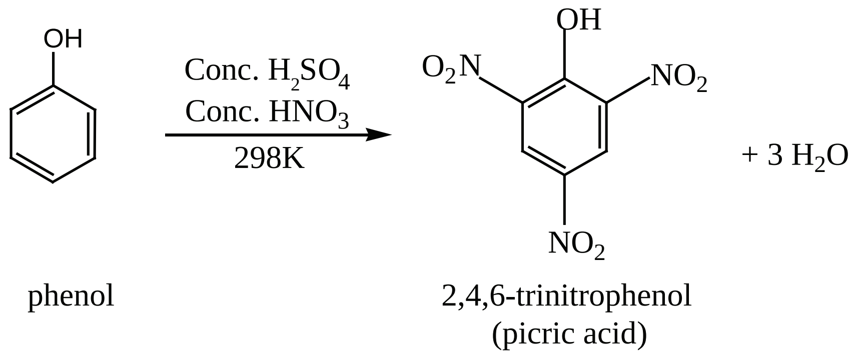


orthonitrophenol
30-40% yield

paranitrophenol
15% yield

The ortho and para isomers are separated by steam distillation, as o-nitro phenol is slightly soluble in water and more volatile due to intra molecular hydrogen bonding, whereas p-nitro phenol is more soluble in water and less volatile due to intermolecular hydrogen bonding.

Nitration with Conc. HNO_3+con.H_2SO_4 gives picric acid.

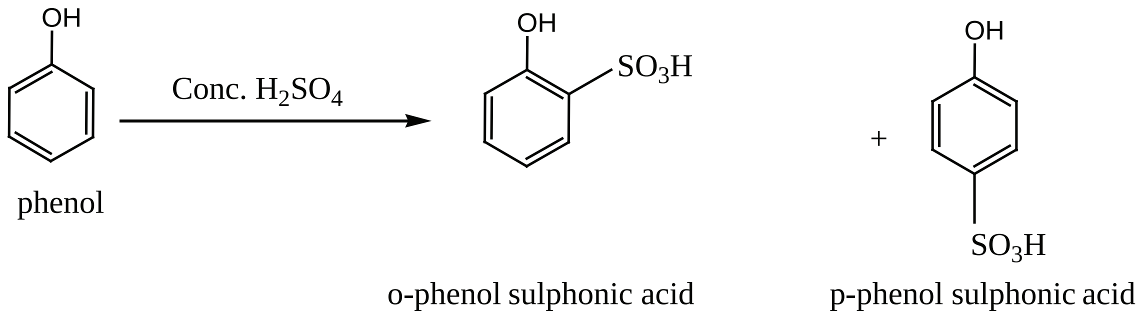


phenol

2,4,6-trinitrophenol
(picric acid)

iii) Sulphonation:

Phenol reacts with con.H_2SO_4 at 280K to form o-phenol sulphonic acid as the major product. When the reaction is carried out at 373K the major product is p-phenol sulphonic acid.



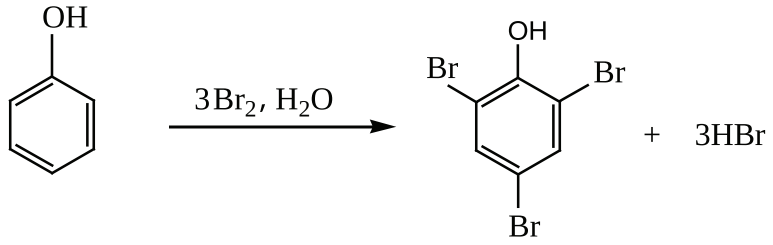
phenol

o-phenol sulphonic acid

p-phenol sulphonic acid

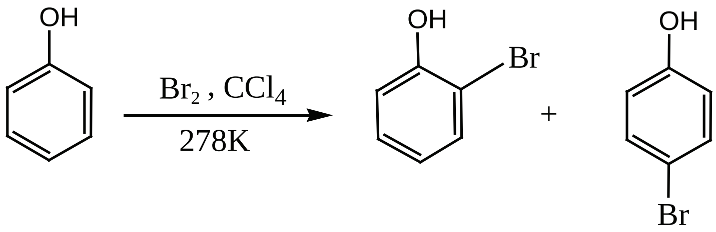
iv) Halogenation:

Phenol reacts with bromine water to give a white precipitate of 2,4,6-tri bromo phenol.



Phenol 2,4,6-tribromophenol

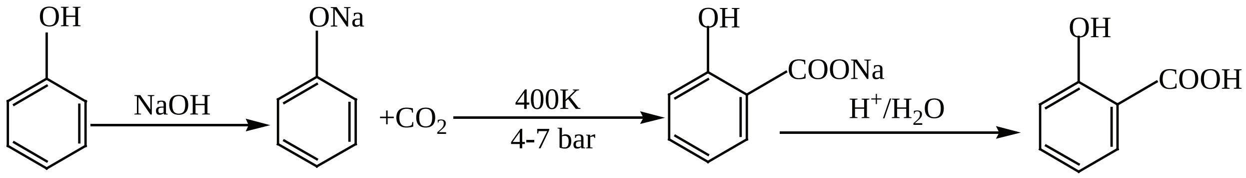
If the reaction is carried out in CS_2 or CCl_4 at 278K, a mixture of ortho and para bromo phenols are formed.



phenol o -bromo phenol p- bromo phenol

v) Kolbe's (or) Kolbe's Schmit reaction:

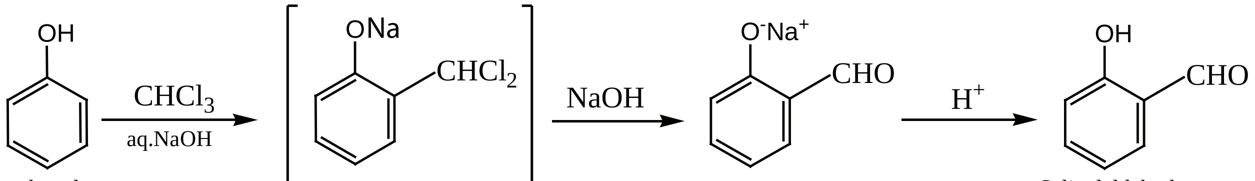
In this reaction, phenol is first converted into sodium phenoxide which is more reactive than phenol towards electrophilic substitution reaction with CO_2 . Treatment of sodium phenoxide with CO_2 at 400K, 4-7 bar pressure followed by acid hydrolysis gives salicylic acid.



phenol sodium phenoxide sodium salicylate Salicyclic acid

vi) Riemer – Tiemann Reaction:

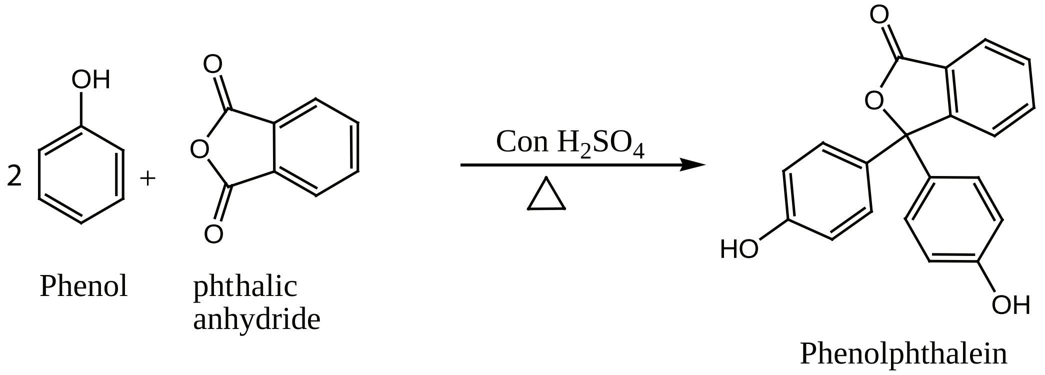
On treating phenol with $CHCl_3$/NaOH, a -CHO group is introduced at ortho position. This reaction proceeds through the formation of substituted benzal chloride intermediate.



phenol Salicylaldehyde

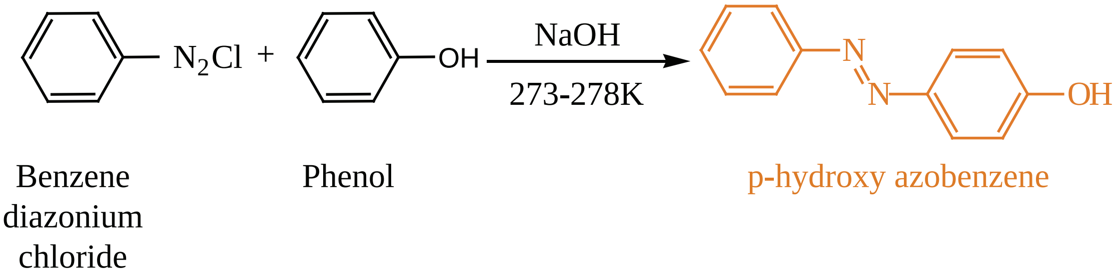
vii) Phthalein reaction:

On heating phenol with phthalic anhydride in presence of con.H_2SO_4, phenolphthalein is obtained.



viii) Coupling reaction:

Phenol couples with benzene diazonium chloride in an alkaline solution to form p-hydroxy azobenzene(a red orange dye).



Test to differentiate alcohol and phenols

i) Phenol react with benzene diazonium chloride to form a red orange dye, but ethanol has no reaction with it.

ii) Phenol gives purple colouration with neutral ferric chloride solution, alcohols do not give such coloration with $FeCl_3$.

iii) Phenol reacts with NaOH to give sodium phenoxide. Ethyl alcohol does not react with NaOH.

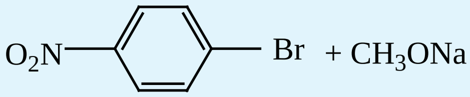
Uses of phenol

1) About half of world production of phenol is used for making phenol formaldehyde resin. (Bakelite).
2) Phenol is a starting material for the preparation of
    - i) drugs such as phenacetin, Salol, aspirin, etc.
    - ii) phenolphthalein indicator.
    - iii) explosive like picric acid.
3) It is used as an antiseptic-carbolic lotion and carbolic soaps.

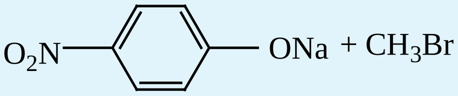
Evaluate Yourself

1. Which of the following set of reactants will give 1-methoxy-4-nitrobenzene.

(i)



(ii)

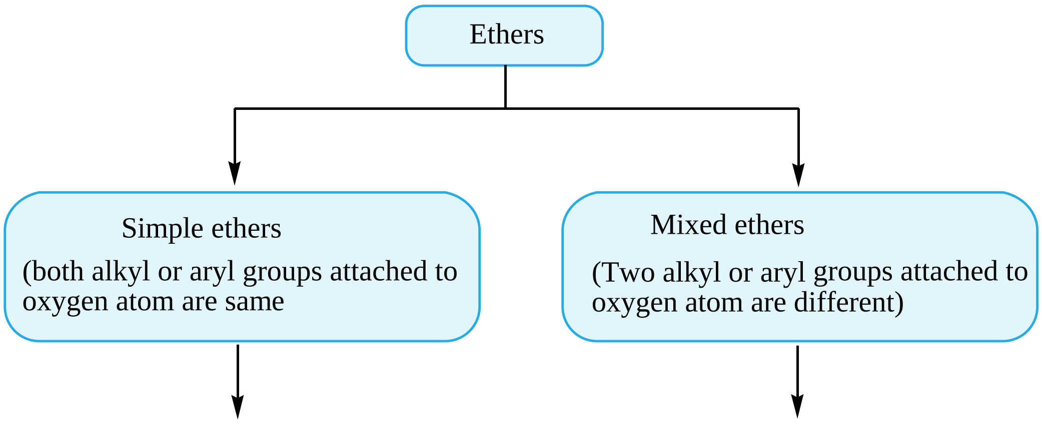


2. what happens when m-cresol is treated with acidic solution of sodium dichromate?
3. when phenol is treated with propan-2-ol in the presence of HF, Friedel-Craft reaction takes place . Identify the products.

Ethers:

Ethers are a class of organic compound in which an oxygen atom is connected to two alkyl/aryl groups ($R - \ddot{\underset{\cdot\cdot}{O}} - R$) . Ethers can be considered as the derivatives of hydrocarbon in which one hydrogen atom is replaced by an alkoxy (-OR) or an aryloxy(-OAr) group. The general formula of aliphatic ether is $C_nH_{2n+2}O$.

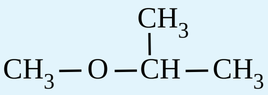
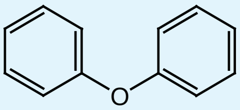
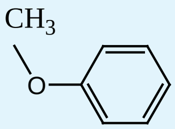
Classification:



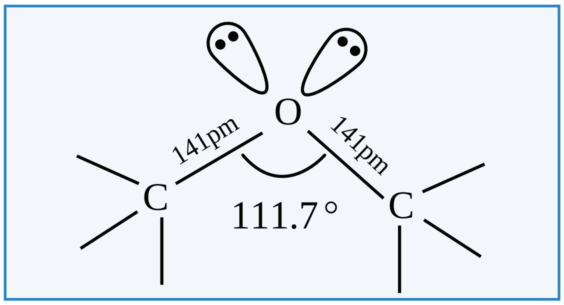
Ethers

Simple ethers
(both alkyl or aryl groups attached to oxygen atom are same

Mixed ethers
(Two alkyl or aryl groups attached to oxygen atom are different)

Aliphatic ethers (Two alkyl groups are attached to etherial oxygen	CH_3-O-CH_3 methoxymethane	 $CH_3-O-\overset{\overset{CH_3}{\vert}}{CH}-CH_3$ 2-methoxypropane
Aromatic ethers Any one (or both) of the group attached to the etherial oxygen is aryl group	 phenoxybenzene	 methoxybenzene

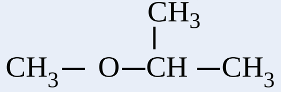
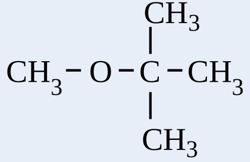
Structure of functional group

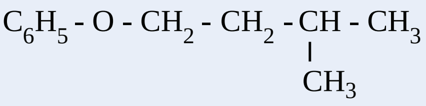


The structure of ethereal oxygen which is attached to two alkyl groups is similar to the structure of -O-H group of alcohol. The oxygen atom is sp^3 hybridized. Two sp^3 hybridized orbitals of oxygen linearly overlap with two sp^3 hybrid orbitals of the carbon which are directly attached to the oxygen forming two C-O'σ' bonds. The C-O-C bond angle is slightly greater than the tetrahedral bond angle due to the repulsive interaction between the two bulkier alkyl groups.

IUPAC System:

Let us recall the naming of ethers according to IUPAC nomenclature.

Compound (Common Name, Structural formula, IUPAC Name)	IUPAC Name			
	Prefix with position number	Root used	Primary suffix	Secondary Suffix
Dimethyl ether CH_3-O-CH_3 Methoxymethane	Methoxy	Meth	ane	–
Isopropyl methyl ether  $CH_3-O-\overset{\overset{CH_3}{\vert}}{C}H-CH_3$ 2-methoxypropane	2-methoxy	prop	ane	–
t-butylmethyl ether  $CH_3-O-\underset{\underset{CH_3}{\vert}}{\overset{\overset{CH_3}{\vert}}{C}}-CH_3$ 2-methoxy-2-methyl propane	2-methoxy 2-methyl	prop	ane	–
Methylphenylether(Anisole) $C_6H_5-O-CH_3$ Methoxybenzene	Methoxy	benzene	–	–
Ethylphenylether(phenetole) $C_6H_5-O-CH_2CH_3$ Ethoxybenzene	Ethoxy	benzene	–	–
Diphenylether or phenylether $C_6H_5-O-C_6H_5$ Phenoxybenzene	Phenoxy	benzene	–	–

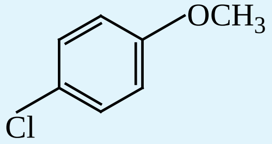
n-heptyl phenyl ether $C_6H_5-O-(CH_2)_6CH_3$ 1-phenoxyheptane	1-phenoxy	hept	ane	–
Isopentylphenylether  $C_6H_5-O-CH_2-CH_2-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH_3$ 3-methyl-1-butoxy benzene	3-methyl-1-butoxy	benzene	–	–
Dimethylglycolate $CH_3-O-CH_2-CH_2-OCH_3$ 1,2-dimethoxyethane.	1,2-dimethoxy	eth	ane	–

Evaluate yourself

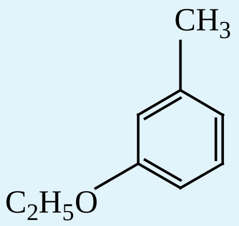
Give the IUPAC name for the following ethers and classify them as simple or mixed.

(i) $CH_3-CH_2-O-(CH_2)_3-CH_3$

(ii)



(iii)



(iv) $(CH_3)_3C-O-C(CH_3)_3$

(v) $CH_2=CH-CH(Cl)-O-CH_3$

(vi) dibenzyl ether

(vii) vinyl allyl ether

Preparation of ethers:

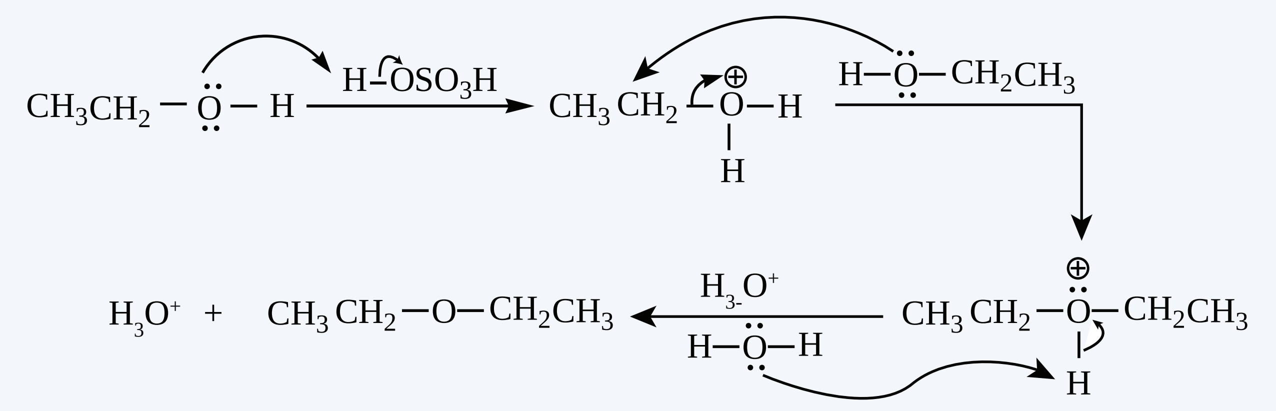
1. Inter molecular dehydration of alcohol.

We have already learnt that when ethanol is treated with con.H_2SO_4 at 443K, elimination takes place to form ethene. If the same reaction is carried out at 413K, substitution competes over elimination to form ethers.

$$\underset{\text{ethanol}}{2CH_3\text{-}CH_2\text{-}OH} \xrightarrow[413K]{H_2SO_4} \underset{\text{diethylether}}{CH_3\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_3}$$

Mechanism:

This method is useful for the preparation of simple ethers and not suitable for preparing mixed ethers. If a mixture of two different alcohols is used, mixture of different ethers will be formed and they are difficult to separate.



2. Williamsons synthesis:

When an alkyl halide is heated with an alcoholic solution of sodium alkoxide, the corresponding ethers are obtained. The reaction involves SN^2 mechanism.

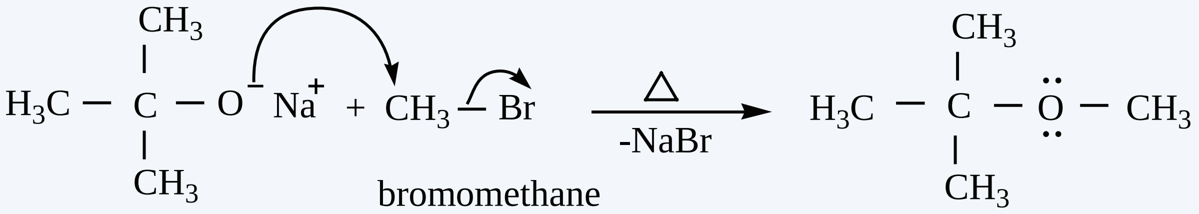
$$CH_3\text{-}ONa + Br\text{-}C_2H_5 \xrightarrow{\Delta} CH_3\text{-}O\text{-}C_2H_5 + NaBr$$

Mechanism:

$$CH_3 - O^-Na^+ + CH_3 - CH_2 - Br \xrightarrow[\Delta]{-NaBr} CH_3 - CH_2 - \ddot{\underset{\cdot\cdot}{O}} - CH_3$$

methoxyethane

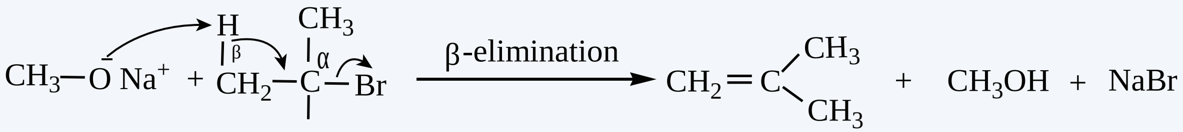
We know that primary alkyl halides are more susceptible for SN^2 reaction. Hence for the preparation of mixed ether having primary and tertiary alkyl group, primary alkyl halide and tertiary alkoxide are used. On the other hand, if we use tertiary alkyl halide and primary alkoxide, elimination dominates and succeeds over substitution to form an an alkene.



bromomethane

2 - methyl - 2- methoxypropane

If tertiary butyl bromide and sodium methoxide are used, 2-methyl prop-1-ene is formed



2-methylprop-1-ene

Methylation of alcohol

Methyl ethers can be prepared by treating an alcohol with diazomethane in presence of catalyst, fluoroboric acid.

$$CH_3\text{-}CH_2\text{-}OH+CH_2N_2 \xrightarrow[\Delta]{HBF_4} CH_3\text{-}CH_2\text{-}O\text{-}CH_3+N_2$$

Evaluate Yourself:

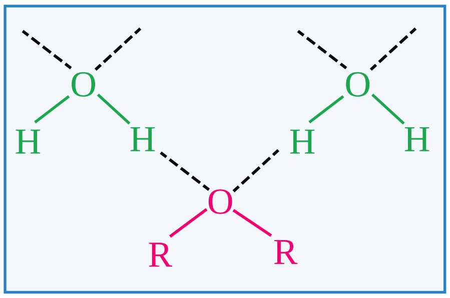
1. Which of the following reaction will give 1-methoxy-4-nitrobenzene.
   a) 4-nitro-1-bromobenzene + sodium methoxide.
   b) 4-nitrosodium phenoxide+bromomethane
2. Arrange the following compounds in the increasing order of their acid strength. propan-1-ol, 2,4,6-trinitrophenol, 3-nitrophenol, 3,5-dinitrophenol, phenol, 4-methylphenol.

Physical Properties:

Ethers are polar in nature. The dipolemoment of ether is the vector sum of two polar C-O bonds with significant contribution from two lone pairs of electrons. For example, the dipole moment of diethyl ether is 1.18D. Boiling point of ethers are slightly higher than that of alkanes and lower than that of alcohols of comparable masses.

Compound	Molar Mass	Boiling point
$CH_3-(CH_2)_5-CH_3$ n-heptane	100.21	371K
$CH_3-O-(CH_2)_4-CH_3$ 1-methoxypentane	102.17	373K
$CH_3-(CH_2)_5-OH$ hexan-1-ol	102.16	430K

Oxygen of ether can also form Hydrogen bond with water and hence they are miscible with water. Ethers dissolve wide range of polar and non-polar substances.



Chemical Properties of ethers:

1. Nucleophilic substitution reactions of ethers.

Ethers can undergo nucleophilic substitution reactions with HBr or HI . HI is more reactive than HBr .

$$CH_3\text{-O-}CH_2\text{-}CH_3 + HI \xrightarrow{\Delta} CH_3I + CH_3\text{-}CH_2\text{-OH}$$

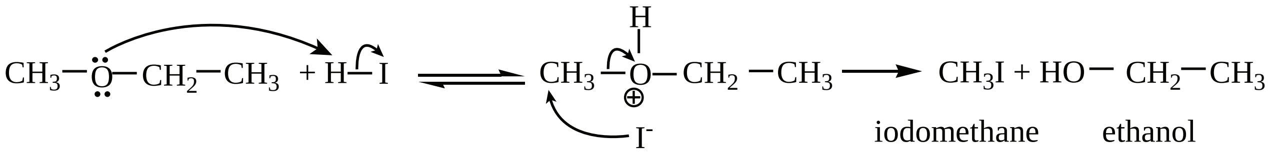
methoxy ethane — iodo methane — ethanol

$$C_6H_5\text{-O-}CH_3 + HI \longrightarrow C_6H_5\text{-OH} + CH_3I$$

methoxy benzene — Phenol — iodomethane

Mechanism:

Ethers having primary alkyl group undergo SN^2 reaction while tertiary alkyl ether undergo SN^1 reaction.Protonation of ether is followed by the attack of halide ion.The halide ion preferentially attacks the less sterically hindered of the two alkyl groups which are attached to etherial oxygen.



When excess HBr or HI is used, the alcohol formed will further react with HBr or HI to form alkyl halides.

$$CH_3\text{-}CH_2\text{-}OH \xrightarrow{\text{excessHBr}} CH_3\text{-}CH_2\text{-}Br$$

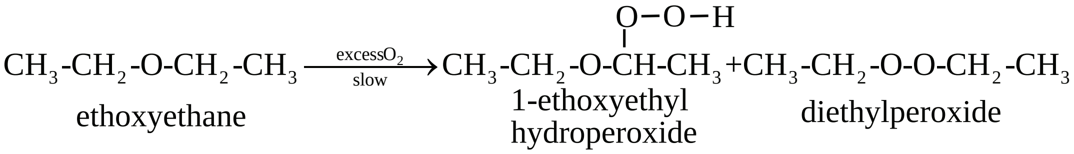
ethanol bromoethane

Evaluate Yourself:

1mole of HI is allowed to react with t-butyl methylether. Identify the product and write down the mechanism of the reaction.

Autooxidation of ethers:

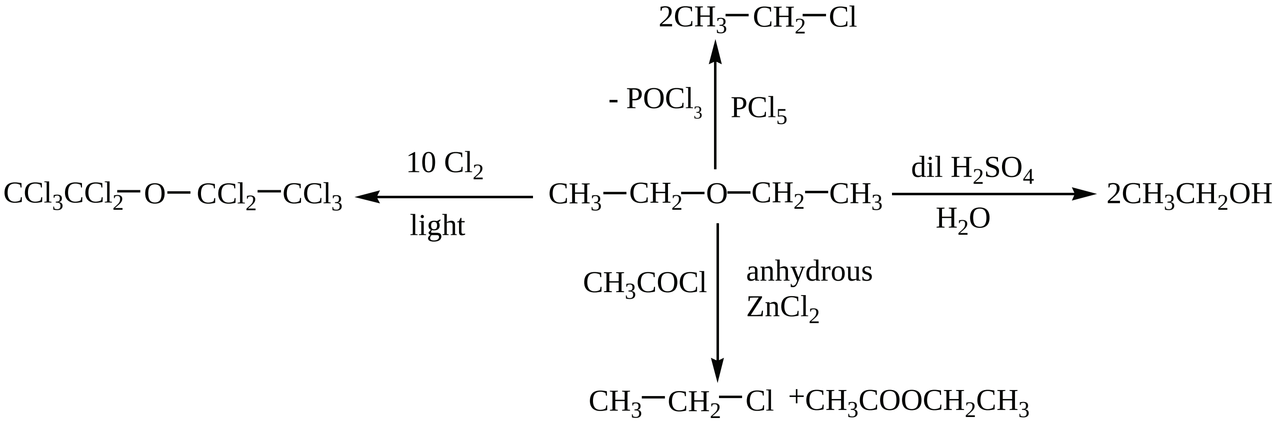
When ethers are stored in the presence of atmospheric oxygen, they slowly oxidise to form hydroperoxides and dialkylperoxides. These are explosive in nature. Such a spontaneous oxidation by atmospheric oxygen is called autooxidation.



$$CH_3\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_3 \xrightarrow[\text{slow}]{\text{excess}O_2} CH_3\text{-}CH_2\text{-}O\text{-}\overset{O-O-H}{\overset{|}{C}H}\text{-}CH_3 + CH_3\text{-}CH_2\text{-}O\text{-}O\text{-}CH_2\text{-}CH_3$$

ethoxyethane 1-ethoxyethyl hydroperoxide diethylperoxide

Some of the reaction of diethyl ether.

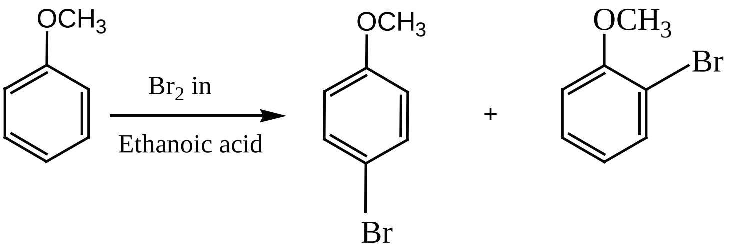


Aromatic electrophilic substitution reactions:

The alkoxy group (-OR) is an ortho, para directing group as well as activating group.It activates the aromatic ring towards electrophilic substitution.

i) Halogenation:

Anisole undergoes bromination with bromine in acetic acid even in the absence of a catalyst, para isomer is obtained as the major product.



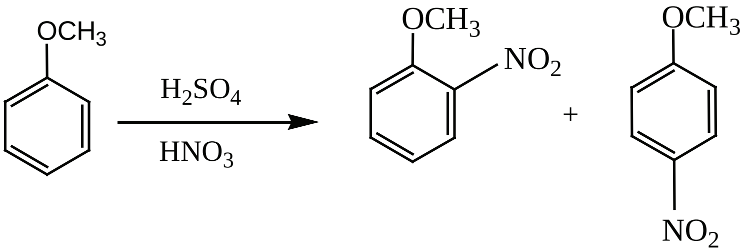
Anisole

p-bromoanisole (major)

o-bromoanisole (minor)

ii) Nitration:

Anisole reacts with a mixture of conc. H_2SO_4/Conc.HNO_3 to yield a mixture of ortho nitro anisole and para nitro anisole.

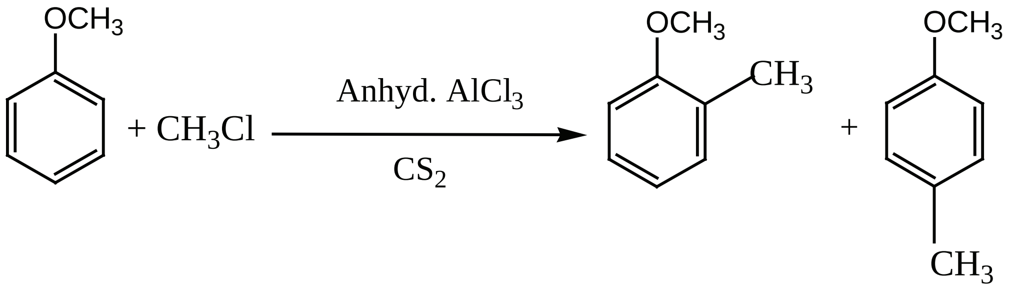


o-nitroanisole (minor)

p-nitroanisole (major)

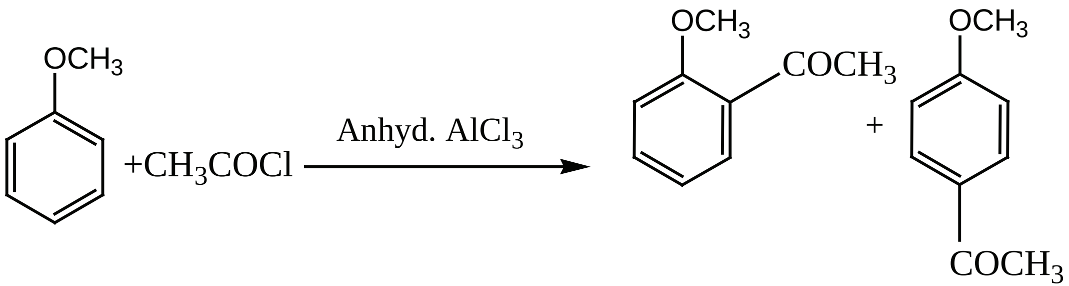
iii) Friedel Craft's reaction:

Anisole undergoes Fridel Craft's reaction in presence of anhydrous $AlCl_3$ as a catalyst.



2-methoxy toluene(minor)

4-methoxy toluene (major)



2-methoxy acetophenone (minor)

4-methoxy Acetophenone (major)

Uses of ethers

Uses of Diethyl ether

1. Diethyl ether is used as a surgical anaesthetic agent in surgery.
2. It is a good solvent for organic reactions and extraction.

3. It is used as a volatile starting fluid for diesel and gasoline engine.
4. It is used as a refrigerant.

Uses of anisole

1. Anisole is a precursor to the synthesis of perfumes and insecticide pheromones,
2. It is used as a pharmaceutical agent .

EVALUATION

Choose the correct answer:

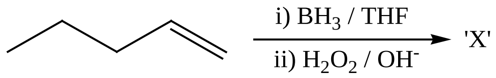
1. An alcohol (x) gives blue colour in Victormeyer's test and 3.7g of X when treated with metallic sodium liberates 560 mL of hydrogen at 273 K and 1 atm pressure what will be the possible structure of X?

a) CH_3 CH (OH) CH_2CH_3 b) $CH_3 - CH (OH) - CH_3$

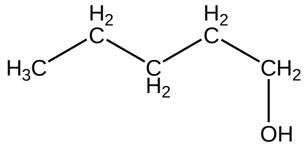
b) CH_3 C (OH) $(CH_3)_2$ d) CH_3- CH_2 –CH (OH) – $CH_2 - CH_3$

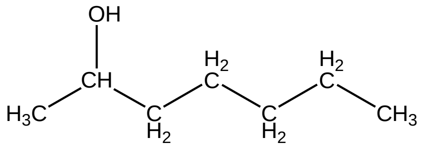
2. Which of the following compounds on reaction with methyl magnesium bromide will give tertiary alcohol.

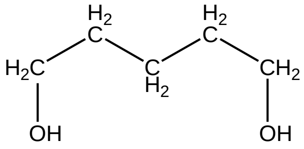
a) benzaldehyde b) propanoic acid c) methyl propanoate d) acetaldehyde

3. 

The X is

a) 

b) 

c) 

d) None of these

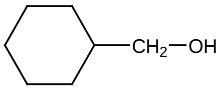
4. In the reaction sequence, Ethene $\xrightarrow{HOCl} A \xrightarrow{X}$ ethan -1, 2 - diol . A and X respectively are

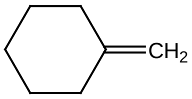
a) Chloroethane and NaOH b) ethanol and H_2SO_4

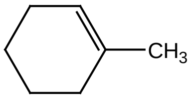
c) 2 – chloroethan -1-ol and $NaHCO_3$ d) ethanol and H_2O

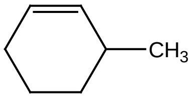
5. Which one of the following is the strongest acid

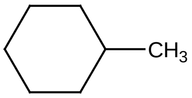
a) 2 - nitrophenol b) 4 – chlorophenol c) 4 – nitrophenol d) 3 – nitrophenol

6.  on treatment with Con H_2SO_4, predominately gives

a) 

b) 

c) 

d) 

7. Carbolic acid is

a) Phenol b) Picric acid d) benzoic acid d) phenylacetic acid

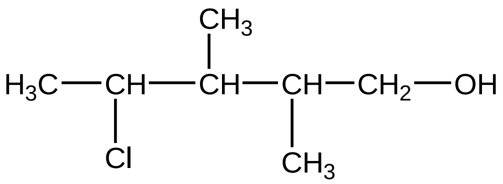
8. Which one of the following will react with phenol to give salicyladehyde after hydrolysis.

a) Dichloro methane b) trichloroethane c) trichloro methane d) CO_2

9. $(CH_3)_3$- C - CH(OH) $CH_3 \xrightarrow{Con\ H_2SO_4}$ X (major product)

a) $(CH_3)_3\ CCH = CH_2$ b) $(CH_3)_2\ C = C\ (CH_3)_2$

c) $CH_2 = C(CH_3)CH_2 - CH_2 - CH_3$ d) $CH_2 = C\ (CH_3) - CH_2 - CH_2 - CH_3$

10. The correct IUPAC name of the compound, 

$H_3C-\underset{Cl}{CH}-\overset{CH_3}{CH}-\underset{CH_3}{CH}-CH_2-OH$

a) 4 – chloro – 2,3 – dimethyl pentan – 1-ol

b) 2,3 – dimethyl – 4- chloropentan -1-ol

c) 2,3,4 – trimethyl – 4- chlorobutan -1-ol

d) 4 – chloro – 2,3,4 – trimethyl pentan – 1-ol

11. Assertion : Phenol is more acidic than ethanol

Reason: Phenoxide ion is resonance stabilized

a) both assertion and reason are true and reason is the correct explanation of assertion.

b) both assertion and reason are true but reason is not the correct explanation of assertion.

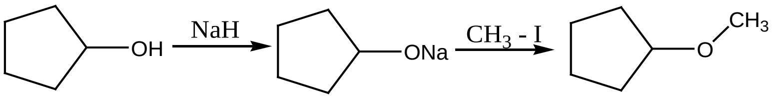
c) assertion is true but reason is false

d) both assertion and reason are false.

12. In the reaction Ethanol $\xrightarrow{PCl_5} X \xrightarrow{alc.KOH} Y \xrightarrow[298K]{H_2SO_4/H_2O} Z$. The 'Z' is

a) ethane b) ethoxyethane c) ethylbisulphite d) ethanol

13. The reaction



Can be classified as

a) dehydration b) Williamson alcoholsynthesis

c) Williamson ether synthesis d) dehydrogenation of alcohol

14. Isopropylbenzene on air oxidation in the presence of dilute acid gives

a) C_6H_5COOH b) $C_6H_5COCH_3$ c) $C_6H_5COC_6H_5$ d) C_6H_5 - OH

15. Assertion : Phenol is more reactive than benzene towards electrophilic substitution reaction

Reason : In the case of phenol, the intermediate arenium ion is more stabilized by resonance.

a) if both assertion and reason are true and reason is the correct explanation of assertion.

b) if both assertion and reason are true but reason is not the correct explanation of assertion.

c) assertion is true but reason is false

d) both assertion and reason are false.

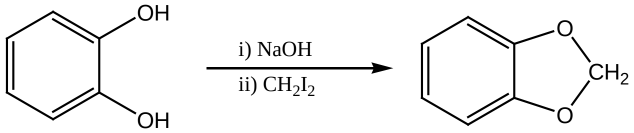
16. HO CH_2 CH_2 – OH on heating with periodic acid gives

a) methanoic acid b) Glyoxal c) methanal d) CO_2

17. Which of the following compound can be used as artifreeze in automobile radiators?

a) methanol b) ethanol c) Neopentyl alcohol d) ethan -1, 2-diol

18. The reactions



is an example of

a) Wurtz reaction b) cyclic reaction c) Williamson reaction d) Kolbe reactions

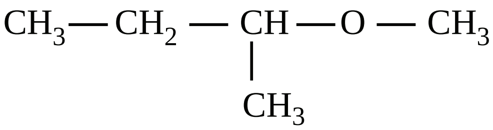
19. One mole of an organic compound (A) with the formula C_3H_8O reacts completely with two moles of HI to form X and Y. When Y is boiled with aqueous alkali it forms Z. Z answers the iodoform test. The compound (A) is

a) propan – 2-ol b) propan -1-ol c) ethoxy ethane d) methoxy ethane

20. Among the following ethers which one will produce methyl alcohol on treatment with hot HI?

a) $(H_3C)_3C-O-CH_3$ b) $(CH_3)_2-CH-CH_2-O-CH_3$

c) $CH_3(CH_2)_3-O-CH_3$ d)



$$CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-O-CH_3$$

21. Williamson synthesis of preparing dimethyl ether is a / an /

a) SN^1 reactions b) SN^2 reaction

c) electrophilic addition d) electrophilic substitution

22. On reacting with neutral ferric chloride, phenol gives

a) red colour b) violet colour c) dark green colour d) no colouration.

Short Answer Questions

1. Identify the product (s) is / are formed when 1 – methoxy propane is heated with excess HI. Name the mechanism involved in the reaction
2. Draw the major product formed when 1-ethoxyprop-1-ene is heated with one equivalent of HI
3. Suggest a suitable reagent to prepare secondary alcohol with identical group using Grignard reagent.
4. What is the major product obtained when two moles of ethyl magnesium bromide is treated with methyl benzoate followed by acid hydrolysis.
5. Predict the major product, when 2-methyl but -2-ene is converted into an alcohol in each of the following methods.

   (i.) Acid catalysed hydration (ii.) Hydroboration

   (iii.) Hydroxylation using Baeyer's reagent
6. Arrange the following in the increasing order of their boiling point and give a reason for your ordering

   (i.) Butan – 2- ol, Butan -1-ol, 2 –methylpropan -2-ol

   (ii.) Propan -1-ol, propan -1,2,3-triol, propan -1,3 – diol, propan -2-ol
7. Can we use nucelophiles such as NH_3,CH_3O^- for the Nucleophilic substitution of alcohols
8. Is it possible to oxidise t – butyl alcohol using acidified dichromate to form a carbonyl compound.
9. What happens when 1-phenyl ethanol is treated with acidified $KMnO_4$.
10. Write the mechanism of acid catalysed dehydration of ethanol to give ethene.
11. How is phenol prepared from

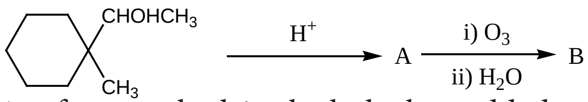
    i) chloro benzene ii) isopropyl benzene
12. Explain Kolbe's reaction
13. Write the chemical equation for Williamson synthesis of 2-ethoxy – 2- methyl pentane starting from ethanol and 2 – methyl pentan -2-ol
14. Write the structure of the aldehyde, carboxylic acid and ester that yield 4- methylpent -2-en-1-ol.
15. What is metamerism? Give the structure and IUPAC name of metamers of 2-methoxy propane
16. How are the following conversions effected

    i) benzylchloride to benzylalcohol ii) benzyl alcohol to benzoic acid
17. Complete the following reactions

i) $CH_3-CH_2-OH \xrightarrow{P\,Br_3} A \xrightarrow{aq.NaOH} B \xrightarrow{Na} C$

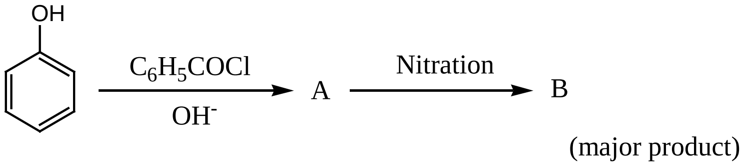
ii) $C_6H_5-OH \xrightarrow{Zn\ dust} A \xrightarrow[Anhydrs\ AlCl_3]{CH_3Cl} B \xrightarrow{acid\ KMnO_4} C$

iii) Anisole $\xrightarrow[AlCl_3]{t\text{-}butylchloride} A \xrightarrow{Cl_2/FeCL_3} B \xrightarrow{HBr} C$

iv) 

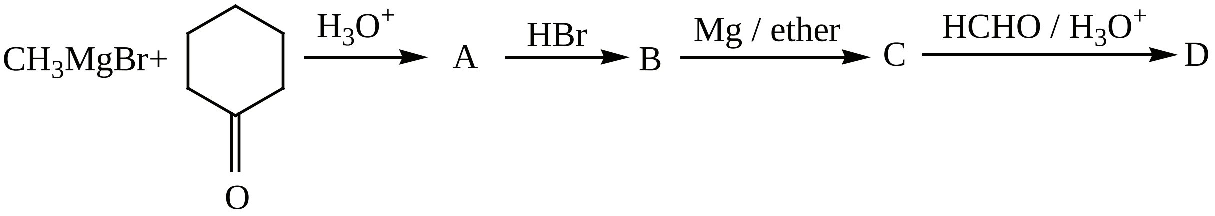
18. 0.44g of a monohydric alcohol when added to methyl magnesium iodide in ether liberates at STP 112 cm^3 of methane with PCC the same alcohol form a carbonyl compound that answers silver mirror test. Identify the compound.

19. Complete the following reactions

i) 

ii) $C_6H_5-CHCH(OH)CH(CH_3)_2 \xrightarrow{ConH_2SO_4}$

20. Phenol is distilled with Zn dust followed by Friedel – Crafts alkylation with propyl chloride to give a compound A, A on oxidation gives (B) Identify A and B.

21. 

Identify A,B,C,D and write the complete equation

22. What will be the product (X and A)for the following reaction

acetylchloride $\xrightarrow[ii)\ H_3O^+]{i)\ CH_3MgBr} X \xrightarrow{acid\ K_2Cr_2O_7} A$

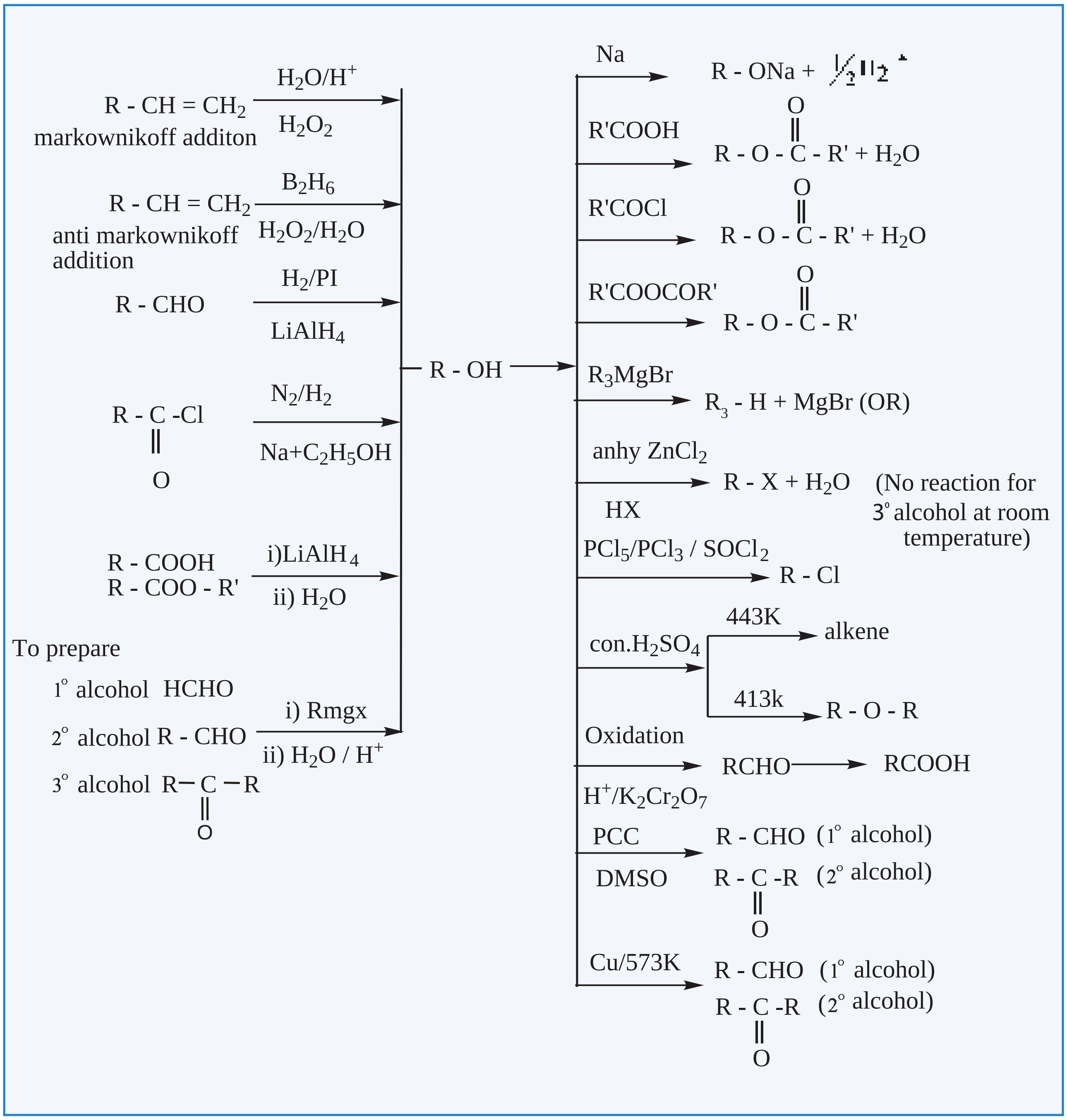
23. How will you convert acetylene into n-butyl alcohol.

24. Predict the product A,B,X and Y in the following sequence of reaction

$$\begin{tikzcd}
\text{butan - 2- ol} \arrow[r, "SOCl_2"] \arrow[d, "Cu / 573K"] & A \arrow[r, "Mg", "ether"'] & B \arrow[d, "X"] \\
X & & Y
\end{tikzcd}$$

25. 3,3 – dimethylbutan -2-ol on treatment with conc. H_2SO_4 to give tetramethyl ethylene as a major product. Suggest a suitable mechanism

ALCOHOL


R - CH = CH2
markownikoff additon
H2O/H+
H2O2
R - CH = CH2
anti markownikoff addition
B2H6
H2O2/H2O
R - CHO
H2/PI
LiAlH4
R - C -Cl
O
N2/H2
Na+C2H5OH
R - COOH
R - COO - R'
i)LiAlH4
ii) H2O
To prepare
1° alcohol HCHO
2° alcohol R - CHO
3° alcohol R-C-R
O
i) Rmgx
ii) H2O / H+
R - OH
Na
R - ONa + ½H2
R'COOH
R - O - C - R' + H2O
R'COCl
R - O - C - R' + H2O
R'COOCOR'
R - O - C - R'
R3MgBr
R3 - H + MgBr (OR)
anhy ZnCl2
HX
R - X + H2O
(No reaction for 3° alcohol at room temperature)
PCl5/PCl3 / SOCl2
R - Cl
con.H2SO4
443K
alkene
413k
R - O - R
Oxidation
H+/K2Cr2O7
RCHO
RCOOH
PCC
DMSO
R - CHO (1° alcohol)
R - C -R (2° alcohol)
Cu/573K
R - CHO (1° alcohol)
R - C -R (2° alcohol)